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# *Cheralite, a new mineral of the monazite group.*

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## *Introduction.*

A GREEN mineral akin to monazite, derived from the State of Travancore in southern India, was investigated chemically during the first world war by the Imperial Institute, London, and was found to be exceptionally rich in thorium and uranium. No description of this unusual 'monazite' has hitherto been published.

The high content of radioactive elements in this mineral led the State Geologist, Mr. Venkitarama Mahadevan, to have a deposit opened up in 1945, in readiness for an assessment of the radioactive mineral resources of Travancore. At the invitation of the former Dewan, Sir C. P. Ramaswami Aiyar, K.C.S.I., K.C.I.E., this assessment was carried out by Dr. C. F. Davidson early in 1946. In an unpublished report to the Dewan, Dr. Davidson records that the mineral in question occurs sparsely distributed throughout a kaolinized pegmatite dike outcropping on a small hill at Kuttakuzhi (lat. 8° 18′ 11″ N., long. 77° 15′ 48″ E.) in Kalkulam taluk, about 23 miles ESE. of Trivandrum. In the pegmatite it is associated with a little black tourmaline, small greenish-yellow crystals of chrysoberyl, partly-metamict dark zircon with a radioactivity equivalent to 0·1 % $U_3O_8$, and considerable smoky-quartz. A few crystals of brown monazite occur in washings from the same pegmatite. The thorium-rich green mineral is also found sparsely in the adjacent wall-rock (kaolinized granitic gneiss) as well as in surface wash and in the gravel of adjacent streams. The occurrence has no economic potentialities, only an ounce or two of 'monazite' being obtainable from

each cubic yard of pegmatite. We are indebted to Dr. Davidson for the material on which this present study is based.

The green mineral has been found to be a member of the monazite group near $(TR,\mathrm{Th,Ca,U})(\mathrm{P,Si})\mathrm{O}_4$ in composition, where $TR$ = Ce, La, Pr, Nd, &c. It is proposed that it be called cheralite from Chera, the ancient Dravidian kingdom which corresponded roughly to the modern territory of Travancore.

*Physical properties.*

Cheralite occurs as brittle masses up to two inches across, seldom showing crystal faces. It is pale to dark green in colour with a resinous to vitreous lustre, an uneven fracture, and a white streak. The hardness is 5, and specific gravity, determined by the pyknometer method in carbon tetrachloride, is $5{\cdot}3 \pm 0{\cdot}1$.

In thin section cheralite is pale green in colour, and it gives a positive biaxial interference figure. The indices of refraction are $\alpha$ 1·779, $\beta$ 1·780, $\gamma$ 1·816. The optic axial angle 2V measured on different fragments of the mineral ranges from 17·4° to 19·0°, the average of some twenty determinations being 18·1°—a figure which is in good agreement with the calculated value of 17·9°. Pleochroism is faint with $\alpha$ and $\beta$ green, $\gamma$ green with a yellow tinge. Dispersion of the optic axes is not perceptible. The cleavage directions and optical orientation appear to be: cleavages (010) distinct, (100) difficult, parting on (001) poor; $\alpha = b$, and $\gamma : c = 7°$. These data are tentative, since it has not been possible to identify the crystal faces on the available material with any certainty.

*Chemical composition.*

The material chosen for analysis was purified by passing the crushed and washed mineral through a Frantz electromagnetic separator, traces of superficial ferruginous matter then being removed by immersion in hot dilute hydrochloric acid. In table I, the new analytical data are compared with an unpublished analysis carried out about 1916 by Mr. S. J. Johnstone of the Imperial Institute, which Mr. G. E. Howling of Colonial Geological Surveys kindly brought to our notice when the present paper was read. Mr. Johnstone's material was collected by Mr. E. Masillamani, then State Geologist, Southern District, Travancore, from a locality described as Cootykad Pothay in Vilavancod taluk —the adjoining taluk (or 'parish') to that from which our specimens were derived. It is uncertain whether there are two localities for the mineral (possibly both on the same pegmatite dike) or whether the

original find was wrongly localized. The material analysed by Mr. Johnstone was not specially purified before analysis and may have been somewhat contaminated by iron and quartz. The other two analyses in table I are of a high-grade monazite concentrate from the Travancore beaches, which form one of the principal commercial sources of this mineral, and of a thorium-rich monazite from Ceylon, which is discussed below.

The recalculation of the new cheralite analysis in terms of atomic proportions (table II) shows that the composition corresponds closely with the formula $ABO_4$, where $A = TR$, Th, Ca, U, and $B =$ P, Si.

TABLE I. Chemical analyses of cheralite and monazite.

| | 1. | 2. | 3. | 4. |
|---|---|---|---|---|
| $P_2O_5$ ... ... | 26·80 | 25·90 | 26·82 | 20·20 |
| $SiO_2$ ... ... | 2·10 | 1·15 | 0·90 | 6·09 |
| $ThO_2$ ... ... | 31·50 | 29·45 | 10·22 | 28·20 |
| $U_3O_8$ ... ... | 4·05 | 6·56 | (0·37) | — |
| $Ce_2O_3$ ... ... | 14·21 | 13·98 | 31·90 | 20·65 |
| $(La,Pr,Nd)_2O_3$ | 13·35* | 13·26 | 28·00 | 21·63 |
| $Yt_2O_3$ | | 0·19 | 0·46 | 0·94 |
| $Fe_2O_3$ ... ... | trace | 2·50 | 1·50 | 1·13 |
| $Al_2O_3$ ... ... | trace | — | 0·17 | 0·29 |
| CaO ... ... | 6·30 | 5·73 | 0·20 | 0·10 |
| PbO ... ... | 0·92 | 0·07 | — | — |
| $H_2O+$ ... | 0·06 | 0·30 | 0·46 | — |
| | 99·29 | 99·59 | 101·00 | 99·23 |

1. Cheralite, Kuttakuzhi, Travancore. Analysis by Radiochemical Division, Chemical Research Laboratory, Teddington. * Major constituents: La, Pr, Nd; minor constituents: Gd, Sm, Yt.
2. 'Green monazite' (= cheralite), from a locality given as 'Cootykad Pothay, Vilavancode taluq, Travancore'. Unpublished analysis by S. J. Johnstone, Imperial Institute, London, 1915 or 1916. Also contains MnO 0·18, $TiO_2$ 0·32 %. Free silica 0·16 % has been omitted.
3. Monazite concentrate from beach sand, Travancore. Analysis by S. J. Johnstone, Journ. Soc. Chem. Indust., 1914, vol. 33, pp. 55–59. Value for $U_3O_8$ by Radiochemical Division, Chemical Research Laboratory, Teddington.
4. Monazite pebble, Ratnapura, Ceylon. Analysis by S. J. Johnstone, ibid. Specific gravity 5·47.

In almost all monazite samples that have been studied chemically, some thorium and a little uranium are present replacing the cerium-lanthanum earths in the crystal lattice of the mineral; but in cheralite this substitution has been carried very much further than in normal monazites. The increase in cationic charge is compensated for by a similarly large substitution of calcium for the cerium-lanthanum earths, aided by the replacement of a little phosphorus by silicon. The result

TABLE II. Analyses of cheralite (table I, 1) and Ratnapura monazite (table I, 4) recalculated as atomic ratios to 16 oxygens.

| Ionic radii (Å.).* | | Cheralite. | | | Ratnapura monazite. | | | |
|---|---|---|---|---|---|---|---|---|
| 0·99 | $Ca^{2+}$ | ... | 1·084 | | $Ca^{2+}$ | ... | 0·018 | |
| 1·07 | $Ce^{3+}$ | 0·836 | | | $Ce^{3+}$ | 1·286 | | |
| 1·14 | $La^{3+}$ | | | | $La^{3+}$ | | | |
| 1·06 | $Pr^{3+}$ | | | | $Pr^{3+}$ | | 2·707 | |
| 1·04 | $Nd^{3+}$ | 0·780 | 1·616 | | $Nd^{3+}$ | 1·335 | | |
| 0·92 | $Yt^{3+}$ | | | 4·030 | $Yt^{3+}$ | 0·086 | | 4·023 |
| 1·02 | $Th^{4+}$ | 1·151 | | | $Th^{4+}$ | ... | 1·092 | |
| 0·97 | $U^{4+}$ | 0·139 | 1·330 | | $U^{4+}$ | — | | |
| 0·80 | $U^{6+}$ | | | | $U^{6+}$ | — | | |
| 1·20 | $Pb^{2+}$ | 0·040 | | | $Pb^{2+}$ | — | | |
| 0·64 | $Fe^{3+}$ | — | | | $Fe^{3+}$ | ... | 0·206 | |
| 0·52 | $Al^{3+}$ | — | | | $Al^{3+}$ | ... | 0·057 | |
| 0·42 | $Si^{4+}$ | ... | 0·337 | 3·979 | $Si^{4+}$ | ... | 1·035 | 4·000 |
| 0·35 | $P^{5+}$ | ... | 3·642 | | $P^{5+}$ | ... | 2·908 | |

* After L. H. Ahrens, Geochim. Cosmochim. Acta, 1952, vol. 2, pp. 155–169.

is that in cheralite the sum of the thorium, uranium, and calcium atoms exceeds the total rare-earth atoms in the ratio of three to two.

Carried to the limit, the replacement of rare earths by calcium and thorium would result in the hypothetical end-member $CaTh(PO_4)_2$, and an attempt was therefore made to synthesize this compound. The synthesis was carried out using thorium orthophosphate, $Th_3(PO_4)_4.4H_2O$, kindly prepared for us by the Radiochemical Division of the Chemical Research Laboratory, mixed in equimolecular proportions with tricalcium orthophosphate, $Ca_3(PO_4)_2$. In one experiment the reagents were fused in an oxygen and coal-gas flame, and in another the mixture was heated in an electric furnace at 1400° C. The product obtained by the latter method was found on X-ray analysis to consist of a single phase isostructural with monazite. In the product of the former experiment, a $ThO_2$ phase was also present, suggesting that dissociation occurs at a high temperature.

In searching the literature relating to monazite, we have only been able to trace one other reliable analysis showing a thoria content comparable to that of cheralite; this is given as analysis 4 in table I, and in terms of atomic proportions in table II. Here the increased cationic charge due to the introduction of thorium is balanced solely by the replacement of phosphorus by silicon, the calcium remaining negligible. The end-member of this type of substitution is the mineral huttonite,

the monoclinic form of $ThSiO_4$. The role of the iron in the analysis of this monazite is uncertain.

It may be mentioned in passing that the 'chemical' age of the cheralite, derived from Wickman's graph,[1] is 492 million years. In the absence of an isotopic analysis of the lead, this apparent age is open to question.

*X-ray powder data.*

Spacings derived from powder photographs of cheralite, of beach-sand monazite from Travancore, and of synthetic $CaTh(PO_4)_2$ are compared in table III with data published by Pabst[2] for monazite from South

TABLE III. X-ray powder data in Å.

| | Monazite South Korea. | | Monazite Travancore. | | Cheralite Travancore. | | $CaTh(PO_4)_2$ Synthetic. | |
|---|---|---|---|---|---|---|---|---|
| *hkl.* | *d.* | Int. | *d.* | Int. | *d.* | Int. | *d.* | Int. |
| $\bar{1}01$ | 5·23 | 4 | — | — | 5·20 | vvw | 5·18 | vvw |
| 110, 011 | 4·72 | 4 | 4·72 | w | 4·68 | w | 4·67 | vw |
| $\bar{1}11$ | 4·17 | 6 | 4·19 | mw | 4·14 | ms | 4·12 | mw |
| 111 | 3·52 | 5 | 3·52 | w | 3·49 | mw | 3·47 | w |
| 200 | 3·31 | 7 | 3·29 | ms | 3·26 | s | 3·24 | s |
| 120 | 3·09 | 10 | 3·10 | vs | 3·07 | vs | 3·05 | vs |
| 210 | 2·99 | 2 | 2·98 | vvw | 2·96 | vvw | 2·94 | vvw |
| $\bar{1}12$, 012 | 2·88 | 7 | 2·87 | m | 2·86 | s | 2·83 | vs |
| $\bar{2}02$ | 2·61 | 2 | 2·62 | vvw | 2·60 | vvw | 2·58 | w |
| $\bar{2}12$, 112 | 2·45 | 3b | 2·46 | vvw | 2·44 | vvw | 2·41 | w |
| | 2·19 | 4 | 2·19 | mw | 2·18 | mw | 2·16 | w |
| | 2·14 | 6 | 2·14 | mb | 2·13 | mwb | 2·11 | mb |
| | 1·969<br>1·963 | 5<br>1 | 1·970 | vw | 1·958 | w | 1·941 | ms |
| | 1·899 | 2b | — | — | — | — | 1·872 | vvw |
| | 1·875 | 6b | 1·874 | mb | 1·870 | mwb | 1·846 | msb |
| | 1·800 | 2 | 1·802 | vvw | 1·795 | vvw | 1·778 | vw |
| | 1·766 | 4 | 1·762 | vvw | 1·758 | vvw | 1·740 | vw |
| | 1·746 | 6 | 1·745 | mwb | 1·733 | mw | 1·718 | ms |
| | 1·695 | 4 | 1·699 | vw | 1·684 | w | 1·667 | mw |
| | 1·651 | 1– | — | — | — | — | 1·629 | vvw |
| | 1·630 | 1– | — | — | — | — | 1·608 | vvw |
| | 1·605 | 1 | 1·606 | vvw | — | — | 1·583 | vvw |
| | — | — | — | — | — | — | 1·556 | vvw |
| | 1·541 | 4 | 1·537 | vvw | 1·534 | vw | 1·517 | mw |

Order of decreasing intensities: vs, s, ms, m, mw, w, vw, vvw; b = broad.

[1] F. E. Wickman, A graph for the calculation of the age of minerals according to the lead method. Årsbok Sveriges Geol. Undersök., 1944, vol. 37, no. 7 (Avhandl. och Upps., Ser C, no. 458), pp. 1–6. [M.A. **9**–69.]

[2] A. Pabst, Huttonite, a new monoclinic thorium silicate. Amer. Min., 1951, vol. 36, pp. 60–65. [M.A. **11**–310.]

Korea. The indices given by Pabst for the first ten powder lines were derived from single-crystal photographs. The powder photographs for the present study were taken in a 9 cm. camera with Cu-$K\alpha$ radiation ($\lambda = 1{\cdot}5418$ Å.) using sodium chloride as an internal standard. The relative intensities were estimated visually.

There is a systematic decrease in corresponding spacings on going from monazite through cheralite to $CaTh(PO_4)_2$; this indicates a shrinkage of the unit cell due to the smaller ionic radii of calcium and thorium compared to cerium and lanthanum. By using the spacings for powder lines representing single reflections, the reciprocal lattices have been computed and the following approximate values thus derived for the unit-cell dimensions:

| | *a*. | *b*. | *c*. | $\beta$. | Vol. |
|---|---|---|---|---|---|
| Monazite, Travancore ... | 6·79 | 7·04 | 6·47 | 104·4° | 299 Å.$^3$ |
| Cheralite, Travancore ... | 6·74 | 7·00 | 6·43 | 104·6° | 294 |
| $CaTh(PO_4)_2$ ... ... | 6·69 | 6·93 | 6·38 | 104·4° | 286 |

The density of cheralite corresponding to the unit-cell contents (table II) and the above dimensions is 5·41 g.cm.$^{-3}$, compared with the measured value of 5·3 g.cm.$^{-3}$.

*Systematic relations.*

The X-ray powder data presented here show that monazite, cheralite, and $CaTh(PO_4)_2$ are isostructural. Huttonite has already been shown by Pabst to possess the same structure. The relationship of cheralite to huttonite and monazite is shown in fig. 1, in which the unit-cell composition of cheralite (see table II) is plotted as point *A* in the monoclinic system $CePO_4$–$CaTh(PO_4)_2$–$ThSiO_4$. In this system cerium and thorium may be in part replaced by other rare earths and by uranium respectively.

It is proposed that the name cheralite be applied to minerals intermediate in composition between monazite and $CaTh(PO_4)_2$, the exact limits of the composition being as indicated in the diagram (fig. 1). The three regions of the diagram for which natural representatives are not yet known or well established are left unnamed.

It will be seen that the Ratnapura mineral plots just outside the field assigned to monazite (point *B*); if further work substantiates the original analysis, it might legitimately be referred to a new species intermediate between monazite and huttonite.

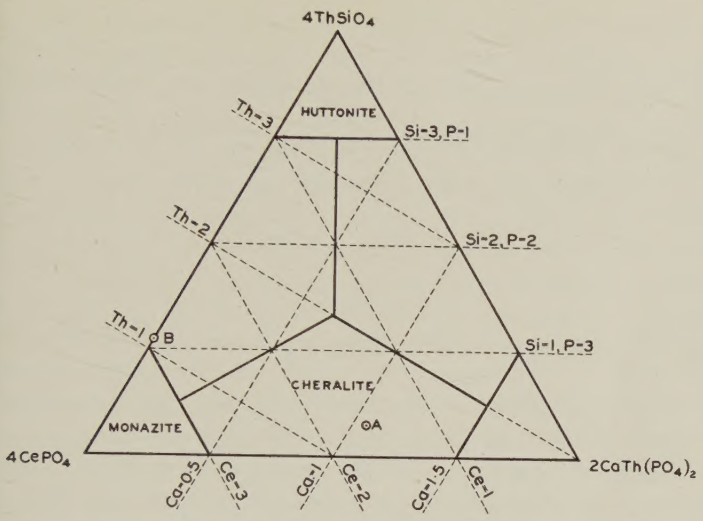


FIG. 1. Relationships in the monoclinic system $CePO_4$–$CaTh(PO_4)_2$–$ThSiO_4$. Point *A*, cheralite, analysis 1; *B*, 'monazite', analysis 4.

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# *The mineralogy of the antimony oxides and antimonates.*

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[Taken as read June 12, 1952.]

## *Introduction*

During an investigation of stibiconite and cervantite (Vitaliano and Mason, 1952) we examined many specimens of antimony ochre. The commonest mineral in these specimens proved to be stibiconite, but others were found, and to establish their identity it became necessary to study the secondary products as a group. The mineralogy of these oxygenated secondary antimony minerals presents unusual problems on account of their earthy and often inhomogeneous nature. Our experience indicates that without X-ray powder photographs it is difficult to establish the true identity of much of this material. The purpose of this paper is to present the results of our investigations and to provide more adequate descriptions of some little-known species.

We would take this opportunity of expressing our appreciation to a number of persons who aided us. Professor C. Frondel of Harvard University, Dr. G. Switzer of the U.S. National Museum, Professor A. Pabst of the University of California, and Dr. H. Neumann of the Mineralogisk Museum in Oslo, made available material from the collections under their care. Dr. D. E. White of the U.S. Geological Survey provided us with a fine collection of secondary antimony minerals from Mexican deposits, which included the new mineral byströmite and material of the rare iron antimonate tripuhyite. Mr. Victor Barua obtained for us specimens of the Peruvian minerals coronguite and arequipite. Numerous spectrographic analyses were made by Mr. R. K. Leininger of the Indiana Geological Survey. Several partial and complete chemical analyses were made by Mr. M. E. Coller. To all these persons our thanks are due.

## *Antimony oxides.*

Senarmontite and valentinite, polymorphs of $Sb_2O_3$, have been known as well-defined minerals for over a century. Senarmontite, although the stable form at ordinary temperatures, is notably rarer than valentinite.

The only senarmontite we have seen came from the type locality, Hamimat near Constantine in Algeria, whereas valentinite occurs at many localities, sometimes in pure state, but more commonly in intimate admixture with stibiconite. The abundance of valentinite contrasted to the rarity of the stable polymorph senarmontite appears to be linked with the presence of foreign ions, as suggested by Bloom (1939) from investigations of synthetic preparations. We checked this by having spectrographic analyses made of senarmontite and of valentinite; whereas the senarmontite was as pure or purer than reagent grade $Sb_2O_3$, showing a trace of arsenic and a slight trace of magnesium only, spectrograms of valentinite showed numerous lines of elements other than antimony.

Valentinite and senarmontite are the only anhydrous oxides of antimony found as minerals. The higher oxides of antimony occur as a hydrated phase of variable composition, which generally contains some calcium. This phase is isometric, with a structure of the pyrochlore type, and a general formula $(Sb^{3+},Ca)_y Sb^{5+}_{2-x}(O,OH,H_2O)_{6-7}$, in which $x$ ranges from 0 almost to 1, and $y$ is generally about 1. Two names, stibiconite and cervantite, have been current for this phase, and since stibiconite has priority we have suggested that this name be retained and that cervantite be dropped. An additional argument for this procedure is that the name cervantite is false in significance, having been specifically applied by its author to anhydrous $Sb_2O_4$, which is not known to occur as a mineral.

The investigation outlined above rendered not only cervantite redundant, but a number of other mineral names also. Hydroroméite, stibianite, and volgerite were found to be identical with stibiconite; arsenostibite is arsenian stibiconite; rivotite proved to be a mixture of malachite and stibiconite; barcenite a mixture of stibiconite and cinnabar; and stibioferrite a mixture of a number of minerals, mainly bindheimite and jarosite.

The definition of stibiconite given above also includes the mineral roméite, which has long been recognized as a calcium antimonate. It is a rare mineral of rather variable composition and has the unfortunate distinction of a remarkably extensive synonymy. Practically every occurrence has been described under a distinct name, and it was not until X-ray techniques were employed that these names were recognized to belong to the same phase. Atopite, schneebergite, weslienite, mauzeliite, and lewisite are all synonyms for roméite (Machatschki, 1932), although some of them may be distinguished as varieties on account of

the presence of sodium or lead proxying for calcium, iron or titanium for antimony, manganese for either, and fluorine for oxygen and hydroxyl. All these minerals occur in metamorphosed ore-deposits, and are generally found as minute yellow or brown octahedra. Stibiconite, on the other hand, is typically the product of supergene alteration of antimony ores, generally occurs as earthy masses, and has never been found as crystals. Nevertheless, there is no essential difference between roméite and stibiconite, either in chemical composition or in crystal-structure. The question as to whether they should be recognized as distinct species we prefer to leave open until such time as some general agreement exists as to the definition of a mineral species.

### *Bindheimite.*

Bindheimite is the common alteration product of lead-antimony sulphides, corresponding in this respect to stibiconite, which is generally the alteration product of stibnite. Like stibiconite, too, it is generally earthy and often impure. The interpretation of published analyses is thus dubious in the absence of proof that the material was homogeneous. We did not attempt to investigate bindheimite thoroughly, since its major characteristics are comparatively well established, but our own data coupled with those in the literature indicate that argentian, cuprian, and calcian varieties exist. Analyses of bindheimite generally report some $Fe_2O_3$, with the remark in some cases that it represents admixed limonite.

The X-ray powder photograph of bindheimite is of the pyrochlore type, and the mineral is thus isostructural with stibiconite. A complete range in composition is presumably possible, but has not been demonstrated. The *d* values for the lines in a powder photograph are reported in table I. The major distinguishing features of the bindheimite pattern from that of stibiconite is the absence of a strong reflection at 5·8–6·0 and the presence of one strong line at 3·03 instead of two lines at 3·07 and 2·95.

Just as stibiconite has its own metamorphic equivalent in roméite, so has bindheimite in the mineral monimolite, described by Igelström in 1865 from Harstig manganese mine in Sweden. Monimolite is essentially a lead antimonate with some substitution of lead by other elements. The powder photograph of monimolite is the same as that of bindheimite, and the lines are rather better defined, evidently as a result of more perfect crystallinity.

The assigning of a suitable formula to bindheimite and monimolite

TABLE I. X-ray powder diffraction data for partzite, bindheimite, and stetefeldtite (Cu-$K\alpha$ radiation; intensities estimated by visual inspection).

| | Partzite. | | Bindheimite.* | | Stetefeldtite. | |
|---|---|---|---|---|---|---|
| *hkl.* | *d.* | Int. | *d.* | Int. | *d.* | Int. |
| 111 | 5·91 | 90 | — | — | — | — |
| 311 | 3·08 | 70 | — | — | — | — |
| 222 | 2·95 | 100 | 3·03 | 100 | 3·02 | 100 |
| 400 | 2·56 | 50 | 2·62 | 60 | 2·61 | 70 |
| 331 | 2·34 | 10 | 2·41 | 10 | — | — |
| 511 | 1·96 | 30 | — | — | — | — |
| 440 | 1·81 | 80 | 1·85 | 80 | 1·85 | 70 |
| 531 | 1·73 | 40 | — | — | — | — |
| 622 | 1·54 | 70 | 1·58 | 80 | 1·58 | 70 |
| 444 | 1·48 | 20 | 1·51 | 30 | 1·51 | 30 |
| 711 | 1·43 | 20 | — | — | — | — |
| 731 | 1·33 | 30 | — | — | — | — |
| 800 | 1·28 | 20 | 1·31 | 20 | 1·31 | 10 |
| 662 | 1·17 | 40 | 1·20 | 40 | 1·20 | 50 |
| 840 | 1·14 | 40 | 1·17 | 40 | 1·17 | 40 |
| 844 | 1·04 | 30 | 1·07 | 40 | 1·07 | 30 |
| 666 | 0·987 | 40 | 1·00 | 40 | 1·00 | 40 |
| 880 | — | — | 0·925 | 10 | — | — |
| 10.6.2 | 0·867 | 40 | 0·884 | 50 | 0·884 | 50 |
| 884 | 0·854 | 20 | 0·872 | 40 | 0·872 | 40 |
| 12.4.0 | — | — | 0·827 | 30 | — | — |
| 10.6.6 | — | — | 0·798 | 40 | — | — |
| 12.4.4 | — | — | 0·788 | 40 | — | — |

* This indexed powder photograph is similar to those previously recorded for bindheimite (ASTM cards, 1950 edition, nos. 2262, 3721, 3811); it is also similar to the ASTM card (no. 3800) for artificial lead antimonate ($2PbO.Sb_2O_5$); however, the ASTM card for monimolite (no. 1372) is quite different, and we believe that the material from which the powder photograph for this card was made must have been wrongly identified.

has been a matter of difficulty, due to the variability shown by chemical analyses. In the course of this research, however, two samples of analysed bindheimite and one of monimolite were obtained for study. The X-ray powder photographs gave a value of 10·47 Å. for the unit-cell dimensions in each of these samples. The analyses were then recalculated in terms of atoms or ions per unit cell. The results are set out in table II. These data indicate that bindheimite and monimolite can be formulated in a similar fashion to stibiconite, as $Pb_ySb_{2-x}O,OH,H_2O)_{6-7}$, in which $x$ can be zero or range toward 1, and $y$ is variable but does not exceed 2. Total $(O,OH,H_2O)$ from the analyses is close to 6, but there is no apparent reason why it could not vary from six to seven. Such a formulation is in agreement with the requirements of the pyrochlore structure.

In view of the lack of optical data on analysed samples of bindheimite the opportunity was taken to measure the refractive indices of the available samples, and the results are incorporated in table II. The refractive index of monimolite is higher than that of our highest immersion liquid, which has an index of 2·06.

TABLE II. Chemical analyses of bindheimite and monimolite, recalculated in terms of atoms per unit cell. ($Fe_2O_3$ deducted as limonite before the recalculation of the analyses.)

| | | 1. | 2. | 3. | | | 1. | 2. | 3. |
|---|---|---|---|---|---|---|---|---|---|
| $Sb_2O_5$ | ... | 43·63 | 44·28 | 38·18 | Sp. gr. | ... | 5·28 | 5·16 | 7·29 |
| PbO | ... | 36·54 | 40·53 | 55·33 | $a$ (Å.) | ... | 10·47 | 10·47 | 10·47 |
| $Fe_2O_3$ | ... | 4·30 | 3·28 | — | $n$ ... | ... | 1·928 | 1·905 | > 2·06 |
| FeO | ... | — | — | 5·57 | | | | | |
| MnO | ... | — | — | 1·16 | Sb ... | ... | 11·4 | 10·8 | 11·8 |
| $H_2O$ | ... | 5·78 | 5·04 | — | Pb | ... | 6·9 | 7·2 | 12·5 |
| insol. | ... | 6·32 | 2·93 | — | Fe ... | ... | — | — | 3·9 |
| | | | | | Mn | ... | — | — | 0·8 |
| | | 96·57 | 96·06 | 100·24 | (O,OH,$H_2O$) | | 47·8 | 44·3 | 46·7 |

1. Bindheimite, Lovelock, Nevada, U.S. Nat. Mus. 86166, E. V. Shannon, Econ. Geol., 1920, vol. 15, p. 92.
2. Bindheimite, San Bernadino Co., California, U.S. Nat. Mus. 87263. E. V. Shannon, ibid., p. 93.
3. Monimolite (type II), Harstig mine, Sweden. Ex Stockholms Högskolas Mineralogiska Institut. G. Flink, Bihang K. Svenska Vet.-Akad. Handl., 1886, vol. 12, part 2, no. 2, p. 40.

Two other minerals which are essentially identical with bindheimite are coronguite and arequipite, both described from Peru by Raimondi (1878). Through the good offices of Mr. Victor Barua, we have received specimens of these minerals from the Raimondi collection of the Museo de la Escuela Nacional de Ingenieros de Perú, the specimens coming from the type localities and presumably identified by Raimondi himself. The coronguite gave an X-ray powder photograph identical with that of bindheimite, and in view of the 7·82 % $Ag_2O$ in the analysis it can be described as an argentian variety of this mineral. Microscopic examination of arequipite showed that it consisted of an intimate admixture of quartz and a yellow isotropic mineral of high refractive index tentatively identified as bindheimite; this was confirmed by an X-ray powder photograph, which showed strong lines of these two minerals. Arequipite is not a silicoantimonate of lead, as Raimondi supposed, but a mixture of bindheimite and quartz.

*Stetefeldtite.*

The name stetefeldtite was proposed by Riotte (1867) for material from the Empire and Philadelphia districts in south-eastern Nevada, where it was being mined at that time as a silver ore. These mining districts are centred on Belmont, a ghost town about 50 miles north-east of Tonopah. Specimens labelled 'stetefeldtite, Belmont, Nye Co., Nevada' were available for study from the collections of the Harvard Mineralogical Museum and of the U.S. National Museum.

The specimen from the U.S. National Museum (104763) showed a yellow powdery material, evidently the stetefeldtite, in a matrix of cavernous quartz. The stetefeldtite was clearly a secondary product, probably after primary sulphides. The Harvard specimen (80285) contained irregular masses of a dull black material occurring together with pyrite in vein-quartz. This black material proved to be stetefeldtite intimately admixed with chalcosine and pyrite; treatment with dilute nitric acid dissolved the sulphides and left the stetefeldtite as a yellow powder similar to the material in the specimens from the U.S. National Museum.

X-ray powder photographs of stetefeldtite are similar to those of bindheimite (table I). Stetefeldtite has the pyrochlore structure and the value of $a$ is 10·46 Å. In view of this close resemblance to bindheimite, the identity of stetefeldtite was checked by spectrographic analysis, which showed that the major metallic elements were antimony and silver. Stetefeldtite is thus essentially a silver antimonate, which agrees with the original analysis, if it assumed that the copper, iron, and sulphur were contributed by admixed chalcosine and pyrite. If the original analysis is recalculated in terms of atoms per unit cell, using 10·46 Å. and a density of 4·6 (measured during this investigation), the result is $Ag_{8\cdot8}Sb_{11\cdot4}(O,OH,H_2O)_{\Sigma 0\cdot6}$. This can be rewritten in a similar form to that of stibiconite and bindheimite, as $Ag_ySb_{2-x}(O,OH,H_2O)_{6-7}$; $y$ is close to 1 in the original analysis, but can presumably vary up to a maximum of 2, while $x$ is about 0·5 in the original analysis.

The refractive index of stetefeldtite, measured on U.S Nat. Mus. 104763, is 1·95. Under the microscope the colour is pale yellow, and grains are isotropic.

*Partzite.*

Partzite was described by Arents (1867) as a mineral formed by the alteration of antimonial sulphide ores in the Blind Spring Hill mining district, Mono County, California. In the same year Blake (1867)

claimed that partzite was actually a mixture, and Ransome (1940), who made a careful study of the mineralogy of the ores of the Blind Spring Hill district, came to much the same conclusion. Under partzite he writes (p. 192):

'A great deal of unsuccessful effort was made to obtain some specimens of the original partzite. Several pieces of what were said to be partzite were obtained from various sources and examined, but no two were alike; and microchemical tests on what seemed to be the best material showed the presence of a large amount of copper and lead, the possibility of some iron, but little else. Tests for antimony were unsuccessful, and the presence of silver was doubtful, certainly not to the reputed extent of the richness credited to it. The polished surface of the so-called partzite showed a definite mixture of mostly oxidized minerals. The positive determination of these was not attempted because of the doubt of its representing the material originally described as partzite.'

Several specimens of partzite from the type locality were available for investigation. Foreign material, mainly quartz and limonite, were present in most specimens, but X-ray powder photographs showed that the dominant mineral in each was a phase with structure and lattice dimensions similar to those of stibiconite (table I). The colour and streak of the purest material is olive-green, but specimens are generally coated with a black tarnish. Spectrographic analyses showed variations from one specimen to another, but the dominant elements in each were copper and antimony; some iron and silver were always present, and calcium varied from a trace up to several per cent. The variability in composition is borne out by variations in density and refractive index; for the three purest specimens the following figures were obtained:

| | Sp. gr. | $n$. |
|---|---|---|
| Harvard (83279) ... | 2·98 | 1·61 |
| Indiana (Z81) ... ... | 3·50 | 1·70 |
| Harvard (80284) ... | 3·96 | 1·82 |

This variability is probably due largely to a varying degree of 'defectness' in the crystal lattice, since similar variations in stibiconite have been shown to be due to this cause.

If the original analysis of partzite is recalculated into atoms per unit cell, using the density (3·8) given by Arents and the figure 10·25 Å. for $a$, the result is $Cu_{9\cdot8}Ag_{1\cdot3}Pb_{0\cdot2}Sb_{7\cdot6}Fe_{0\cdot8}(O,OH,H_2O)_{41\cdot5}$ or, including Ag and Pb with Cu, and Fe with Sb, $Cu_{11\cdot3}Sb_{8\cdot4}(O,OH,H_2O)_{41\cdot5}$. Partzite can be interpreted as a hydrated copper antimonate with the pyrochlore structure and a formula similar to other minerals of this type, i.e., $Cu_ySb_{2-x}(O,OH,H_2O)_{6-7}$, in which $y$ has a maximum value of 2 but can be less, and $x$ is between 0 and 1. The agreement of the analysis with this formula is not good, but the structural and other analogies of

partzite with stibiconite and other minerals of this type favour the formula adopted, and it is probable that the original analysis is somewhat in error.

*Byströmite.*

We have recently (1952) described byströmite, a magnesium antimonate from El Antimonio, Sonora, Mexico. An interesting feature is that this is the first antimonate with the trirutile structure to be recognized as a mineral, although synthetic antimonates of this type have been known for some years. We have since found that the iron antimonates tripuhyite and flajolotite also have this structure. It is not unlikely that other antimonate minerals of this structure type will be found, since studies on synthetic compounds have shown that metals with ionic radii between 0·6 Å. and 0·9 Å. form antimonates of this kind.

*Tripuhyite.*

Iron antimonates have been known as minerals for many years; tripuhyite was named by Hussak and Prior in 1897, flajolotite by Lacroix in 1910. Nothing has been known as to their crystallography, since tripuhyite was found as fragments in alluvial deposits, and flajolotite occurs only as fine-grained earthy masses. The discovery of byströmite provided the clue for the elucidation of tripuhyite and flajolotite; comparison of X-ray powder photographs of the three minerals showed that all had similar structures. It has also resulted in the finding of another locality for tripuhyite; while examining antimony ore from El Antimonio, Sonora, Mexico, we found some specimens of a dark brown to black substance which proved to be that mineral. It is present in specimens from the Palo Verde and Argentina mines, and the mineral is probably not uncommon at El Antimonio. We have since recognized by means of powder photographs that the brown or black colour of some stibiconites is generally due to the presence of admixed tripuhyite; such admixture has been recognized in material from near Taxco, Guerrero, Mexico, and from Losacio in Spain.

The tripuhyite from El Antimonio is always very fine-grained, and shows no trace of crystal form or cleavage. The colour is dark brown or black, the streak dark brown with a greenish tinge. The hardness is about 7. The density of the analysed material, determined by a modification of the Penfield method (Mason, 1944), is 3·99, which when corrected for the presence of 36 % quartz gives a density of 5·6 for the tripuhyite.

Specimens of tripuhyite from El Antimonio are so nearly opaque, even in the thinnest grains, that it has not been possible to measure the refractive indices. In part at least this opacity is due to minute inclusions. The same is true for material of flajolotite from Algeria. For optical data we can therefore do no more than quote from E. S. Larsen's report (1921) on tripuhyite from the type locality in Brazil: 'Greenish-yellow grains. Optically +, 2V small, $\rho < v$ (very strong); $\alpha = 2{\cdot}19 \pm 0{\cdot}01$, $\beta = 2{\cdot}20 \pm 0{\cdot}01$; $\gamma = 2{\cdot}33 \pm 0{\cdot}01$.' Evidently the tripuhyite from Brazil is anomalously biaxial.

TABLE III. X-ray powder diffraction data for tripuhyite. (Cu-$K\alpha$ radiation; intensities estimated by visual inspection.)

| *hkl.* | *d*(Å.). | Int. | *hkl.* | *d*(Å.). | Int. | *hkl.* | *d*(Å.). | Int. |
|---|---|---|---|---|---|---|---|---|
| 101 | 4·23 | 20 | 116 | 1·39 | 20 | 406 | 0·921 | 10 |
| 110 | 3·28 | 100 | 303 | 1·38 | 30 | 219 | 0·914 | 20 |
| 103 | 2·56 | 90 | 206 | 1·28 | 10 | 510 | 0·908 | 10 |
| 200 | 2·32 | 40 | 323 | 1·19 | 20 | 336 | 0·888 | 10 |
| 113 | 2·24 | 20 | 400 | 1·16 | 10 | 503 | 0·885 | 20 |
| 210 | 2·08 | 10 | 226 | 1·12 | 20 | 426 | 0·857 | 20 |
| 202 | | | 330 | 1·09 | 10 | 309 | 0·849 | 10 |
| 213 | 1·72 | 90 | 316 | 1·06 | 20 | 523 | 0·827 | 30 |
| 220 | 1·64 | 50 | 413 | 1·05 | 20 | 329 | 0·797 | 10 |
| 006 | 1·52 | 30 | 420 | 1·03 | 10 | 516 | 0·782 | 20 |
| 310 | 1·47 | 40 | 109 | 0·993 | 10 | | | |

Table III gives the data for the X-ray powder photograph of tripuhyite. The lines are indexed on the basis of a tetragonal unit cell, with dimensions $a$ 4·63, $c$ 9·14 Å. On this basis the structure is of the trirutile type, and tripuhyite is isostructural with byströmite and tapiolite ($FeTa_2O_6$). The identification of the structure as of the trirutile type rests on the very weak (101) reflection; otherwise the powder photograph could be completely indexed on a cell of the simple rutile type, with a value for $c$ one-third that given above.

The analysis of tripuhyite in table IV was carried out in the following way. A weighed sample was dissolved in concentrated HCl to which KI had been added as a reducing agent, the solution diluted slightly, and the undissolved material filtered off and ignited. The ignited residue was examined microscopically and found to be quartz grains with numerous inclusions of tripuhyite. The antimony was precipitated from the filtrate by $H_2S$. $NH_4OH$ was then added to the solution to precipitate Fe, Al, and Ti. Iron was determined by titration with $KMnO_4$, Ti estimated colorimetrically, and the $Al_2O_3$ computed by difference. Calcium was tested for but not found; magnesium was precipitated as phosphate. Antimony was determined on a separate sample dissolved

TABLE IV. Chemical analysis of tripuhyite from El Antimonio, Sonora, Mexico.

| | | 1. | | | 2. |
|---|---|---|---|---|---|
| Sb | ... | 34·3 | $Sb_2O_5$ | ... | 70·3 |
| Fe | ... | 10·71 | $Fe_2O_3$ | ... | 23·6 |
| O | ... | 16·8 | | | — |
| $TiO_2$ | ... | 1·34 | | | 2·1 |
| $Al_2O_3$ | ... | 1·48 | | | 2·3 |
| CaO | ... | nt. fd. | | | — |
| MgO | ... | 0·14 | | | 0·2 |
| $H_2O+$ | ... | 0·98 | | | 1·5 |
| $HO_2-$ | | 0·34 | | | — |
| insol.* | ... | 36·0 | | | — |
| | | 102·09 | | | 100·0 |

1. Analysis of mixture of tripuhyite and quartz.
2. Same, recalculated to 100 after deducting quartz, with Sb as $Sb_2O_5$ and Fe as $Fe_2O_3$.

* Quartz with tripuhyite inclusions.

as before; the antimony was precipitated as the sulphide, and the precipitate redissolved by digestion with concentrated $H_2SO_4$ and $Na_2SO_4$ in a Kjeldahl flask. The solution thus obtained was reduced with $Na_2SO_3$ and the antimony titrated with standard $KMnO_4$ solution at 5° C. Combined water was determined by the Penfield method. Reducible oxygen was determined by igniting the mineral in a stream of purified hydrogen at 850° C. and absorbing and weighing the water thus formed. Allowance was made for the water content of the mineral. The reducible oxygen exceeds slightly the amount required for trivalent iron and quinquivalent antimony, and this excess is probably due in part to the oxygen equivalent to titanium. However, most of the discrepancy probably results from incomplete solution giving low values for iron and antimony compared with complete breakdown of the material on ignition in a stream of hydrogen. This factor is responsible also for the high summation of the analysis as a whole.

In table V the analysis of the tripuhyite from El Antimonio is compared with the original analyses of tripuhyite from Brazil and flajolotite from Algeria. The analyses are recalculated into atoms per unit cell, using the cell dimensions given above and the measured densities. Structural considerations predict that the ideal unit-cell content should be $Fe_3Sb_3O_{12}$, and experience with other antimony oxide minerals suggests the possibility of defect lattices. The results set out in table V support these ideas, except for the analysis of the original tripuhyite from Brazil, for which oxygen appears deficient. However, if the iron

TABLE V. Chemical analyses of tripuhyite and flajolotite, recalculated in terms of atoms per unit cell.

| | 1. | 2. | 3. | | 1. | 2. | 3. |
|---|---|---|---|---|---|---|---|
| $Sb_2O_5$ ... | 66·68 | 70·3 | 63·5 | Sb. ... ... | 2·9 | 2·8 | 2·2 |
| $Fe_2O_3$ ... | — | 23·6 | 31·4 | Fe ... ... | 2·7 | 1·9 | 2·3 |
| FeO ... | 27·70 | nt. fd. | — | Ti ... ... | 0·1 | 0·2 | — |
| $TiO_2$ ... | 0·86 | 2·1 | — | Al ... ... | 0·2 | 0·3 | — |
| $Al_2O_3$ ... | 1·40 | 2·3 | — | Mg ... ... | — | 0·03 | — |
| MgO ... | — | 0·2 | — | Ca ... ... | 0·1 | — | — |
| CaO ... | 0·82 | nt. fd. | — | $(O,OH,H_2O)$ ... | 10·6 | 11·9 | 11·8 |
| $H_2O$ ... | — | 1·5 | 5·1 | | | | |
| | 98·81 | 100·0 | 100·0 | | | | |
| Sp. gr. ... | 5·8 | 5·6 | 5·1* | | | | |

* Determined on a specimen from the U.S. National Museum (94635).

1. Tripuhyite, Tripuhy, Brazil. Total includes $SiO_2$ 1·35. (Hussak and Prior 1897.)

2. Tripuhyite, El Antimonio, Sonora, Mexico. (New analysis.)

3. Tripuhyite (Flajolotite), Hammam N'bail, Algeria. Analysis by — Flajolot (quoted by A. Lacroix, 1910).

in the Brazilian tripuhyite is assumed to be trivalent, the unit-cell content will be $(Fe,Ti,Al,Ca)_{3\cdot1}Sb_{2\cdot9}O_{11\cdot9}$, close to the ideal formula. Actually, in Prior's original analysis the iron was assumed to be in the ferrous state, but no proof of this was given, and when calculated on this basis the analysis agrees reasonably well with the formula $Fe_2Sb_2O_7$ ($2FeO.Sb_2O_5$). However, a formula of this type is improbable for a substance with the trirutile structure; it should be either $FeSb_2O_6$ ($FeO.Sb_2O_5$) or $Fe_2Sb_2O_8$ ($Fe_2O_3.Sb_2O_5$), or some variant of these. The recalculation of Prior's analysis on the assumption of the iron being in the ferric state shows good agreement with the latter formula. Supporting evidence for this assumption is provided by the dimensions of the unit cell; the unit cell of tripuhyite is smaller than that of byströmite, whereas if tripuhyite were a ferrous antimonate one would expect the unit cell to be larger, since the ferrous ion is larger than the magnesium ion. The ferric ion being smaller than the magnesium ion allows for the observed diminution in the volume of the unit cell.

On these grounds, therefore, it seems that Prior's assumption that in tripuhyite the iron is in the ferrous state is not justified, and that tripuhyite should be formulated $Fe_2O_3.Sb_2O_5$ ($FeSbO_4$) rather than $Fe_2Sb_2O_7$. However, on this basis there is no significant difference between tripuhyite and flajolotite. They have the same structure, as shown by X-ray powder photographs, and essentially the same chemical composition. The analysis of flajolotite shows the presence of water in

he mineral, which represents hydroxyl groups replacing oxygen in the tructure and thereby balancing a deficiency in cations.

We therefore believe that the ideal formula of tripuhyite is $FeSbO_4$ nd that a deficiency in cations is possible (such as we have demonstrated for byströmite), so that actual analyses may correspond to a ormula of the type $Fe_{1-y}Sb_{1-x}(O,OH)_4$, the $x$ and $y$ indicating possible defectness' in the lattice. When tripuhyite is defined in this way it ncludes flajolotite, and since tripuhyite has priority, the name flajolite should be relegated to the synonymy.

## *Summary.*

The mineralogy of the antimony oxides and antimonates is summarized in table VI. Apart from the polymorphs of $Sb_2O_3$, senarmontite

TABLE VI. Mineralogy of the antimony oxides and antimonates.

| | | |
|---|---|---|
| Senarmontite ... | $Sb_2O_3$ | Cubic |
| Valentinite ... | $Sb_2O_3$ | Orthorhombic |
| Stibiconite ... | $(Sb^{3+},Ca)_ySb_{2-x}(O,OH,H_2O)_{6-7}$ | Cubic |
| Bindheimite ... | $Pb_ySb_{2-x}(O,OH,H_2O)_{6-7}$ | ,, |
| Stetefeldtite ... | $Ag_ySb_{2-x}(O,OH,H_2O)_{6-7}$ | ,, |
| Partzite ... ... | $Cu_ySb_{2-x}(O,OH,H_2O_{6-7}$ | ,, |
| Tripuhyite ... ... | $Fe_{1-y}Sb_{1-x}(O,OH)_4$ | Tetragonal |
| Byströmite ... | $Mg_{1-y}Sb_{2-x}(O,OH)_6$ | ,, |

nd valentinite, they fall into two structural groups, a cubic group vith the pyrochlore structure and a tetragonal group with the trirutile tructure. When the antimony is associated with large cations the yrochlore structure is stable; with smaller cations the trirutile structure is the stable form. Defect lattices are usual in these minerals, esulting in great variability of chemical composition and in physical nd optical properties within the individual species.

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# *The pumpellyite mineral series.*

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## Introduction.

THE bluish-green epidote-like mineral, pumpellyite, was first described by Palache and Vassar (1925) from the copper-bearing amygdaloidal lavas of the Lake Superior region. It has since been reported from many parts of the world in rocks which have undergone low grades of metamorphism, especially types such as amygdaloidal spilites and diabases (Burbank, 1927; Waldmann, 1934; Tsuboi, 1936; Quitzow, 1935, 1936; Klein, 1939; Lacroix, 1942; Sæther, 1942; Zavaritsky, 1944; Korzhinsky, 1944; de Roever, 1947a, b; Kvasha, 1950) and in glaucophane-schists and even eclogites in which pumpellyite is often associated with lawsonite (Irving, Vonsen, and Gonyer, 1932; Quitzow, 1935, 1936; Lacroix, 1942; Switzer, 1945; de Roever, 1947a, b, 1950). W. P. de Roever (1947a, 1950) has suggested a pumpellyitic facies of metamorphism as a lower-grade equivalent of his lawsonite-glaucophane subfacies, characterized by high confining pressure, but subordinate shearing stress and thermal influence, and passing into unmetamorphosed rocks. Nevertheless, pumpellyite can certainly form under conditions of strong shearing stress accompanied by relatively low temperatures (Hutton, 1937; Amies, 1950).

Pumpellyite is widespread in southern New Zealand and has been described from the less highly metamorphosed rocks of the chlorite zone by Hutton (1937, 1940), Turner (1939), Amies (1950), and Reed (1950).

Professor C. E. Tilley has kindly allowed the writer to examine material collected by him from amygdaloidal pillow lavas at Howell's Point, Southland. The present writer has found that in the Taringatura district of Southland the mineral occurs with albite in the lower members of a thick series of tuffaceous greywackes which are quite unmetamorphosed apart from such changes as zeolitization of vitric tuffs and albitization of plagioclase. Some of this Taringatura pumpellyite has hitherto unrecorded optical properties.

In spite of the wide distribution of pumpellyite, knowledge of its crystallography has been very scanty. This is undoubtedly due to a tendency towards unusually poor crystal development. All observers have noticed elongation parallel to the *b* crystal axis (optical $\beta$) and although Palache and Vassar thought that the mineral was probably orthorhombic, its monoclinic nature was correctly deduced by Burbank (1927). Several writers have reported a good cleavage in the zone of the *b*-axis and they have tentatively considered it as a basal cleavage. It appears from the present work that the basal plane of Irving, Vonsen and Gonyer, and of Tsuboi (herein adopted) is not that of other workers such as Palache and Vassar, Burbank, Quitzow, Korzhinsky, and de Roever.

J. E. de Villiers (1941) made a careful study of the optical and crystallographic properties of a fairly well-crystallized mineral from Johannesburg which he considered to be pumpellyite, but the inter-cleavage angle (65–70°) does not agree with that found in the present study (82·4°), and optical properties of the Johannesburg mineral are notably discordant from those of all proven pumpellyites. It is clear that de Villiers was working with some other mineral, and his paper will not be referred to further.

Knowledge of the optical properties has been a little more detailed than that of the morphology of pumpellyite, but it is still far from complete. The orientation of the $\alpha$ and $\gamma$ optical directions with respect to the 'basal plane' as recorded by Vonsen and co-workers and by Tsuboi contrast sharply with that described by the other workers quoted above. One major discrepancy was recently removed when Nel, Strauss, and Wickman (1949) proved that the mineral noted by Söhnge (1945) as 'pumpellyite (?)' is a new species, lombaardite, with a distinctive X-ray powder pattern. In view of our rather limited knowledge of pumpellyite, an X-ray and optical study has been undertaken of all available material, and some new partial chemical analyses have been performed.

### Determination of cell-size and space-group.

Through the courtesy of Dr. F. A. Bannister a small fragment of a specimen in the British Museum (B.M. 1926,226), was made available for study. It was originally forwarded to the Museum by Professor Palache and comes from his type locality in the Lake Superior region, Calumet and Hecla mine, Houghton County, Michigan. The fragment consists of an aggregate of small epidote crystals on matrix, some of the epidote carrying a bluish-green dusting of tiny bladed needles of pumpellyite. The specimen had been treated with dilute hydrochloric acid to remove calcite. Microscopic examination proved that the pumpellyite needles are sub-parallel and distorted growths, and they are heavily striated parallel to the length. Several of the more homogeneous-looking grains were set up for oscillation photographs about their long axes. All gave streaks along the powder rings, but one lath-shaped grain, $0{\cdot}27 \times 0{\cdot}09 \times 0{\cdot}04$ mm., gave two or three maxima in each streak sufficiently well defined to allow interpretation. This crystal was used for zero-layer normal-beam and first and second layer-line equi-inclination Weissenberg photographs with the crystal oscillating about the *b*-axis (fig. 1). Exposures of up to 90 hours were required using filtered Cu-$K\alpha$ radiation. Although lattice planes are represented in the photographs by long streaks, maxima are well defined and the streaks themselves are very narrow, allowing accurate measurement of $\xi$ values, both for $K\alpha_1$ and $K\alpha_2$ reflections. Between the maxima the streaks are continuous, indicating twisting of lattice planes about the *b*-axis.

The cell-edge *b* was estimated from Cu-$K\alpha$ and Cu-$K\beta$ layer-lines in oscillation photographs as 5·95 and 5·97 Å. respectively. Using the provisional value so obtained together with values of *a*, *c*, and $\beta$ obtained as below, lattice spacings were calculated for planes giving strong spots on the Weissenberg photographs. In this way many of the lines on a 19-cm. powder photograph were successfully indexed. Systematic discrepancies between observed and calculated powder line spacings of the forms (02*l*), (*h*2*l*) led to the refined value *b* 5·94 Å. The dimensions *a*, *c*, and $\beta$ were determined from high-angle reflections in the zero-level Weissenberg photographs, with the probable limits of error listed in the tabulation below. The unit cell chosen is *A*-face-centred, $\beta$ 97·6°. This choice of cell emphasizes relationships with the epidote group and also with lawsonite. It accords with the choice of basal plane by Irving, Vonsen, and Gonyer, and by Tsuboi, but not with that of the other

workers, which becomes {100}. The wave-lengths used in the calculations were Cu-$K\alpha = 1{\cdot}540$ Å., Cu-$K\beta = 1{\cdot}544$ Å. The Calumet pumpellyite cell is as follows:

$a$ $8{\cdot}81 \pm 0{\cdot}02$, $b$ $5{\cdot}94 \pm 0{\cdot}01$, $c$ $19{\cdot}14 \pm 0{\cdot}02$ Å., $\beta = 97{\cdot}6° \pm 0{\cdot}2°$.

Some difficulty in the interpretation of the oscillation photographs was caused by the presence of streaked spots falling irregularly between

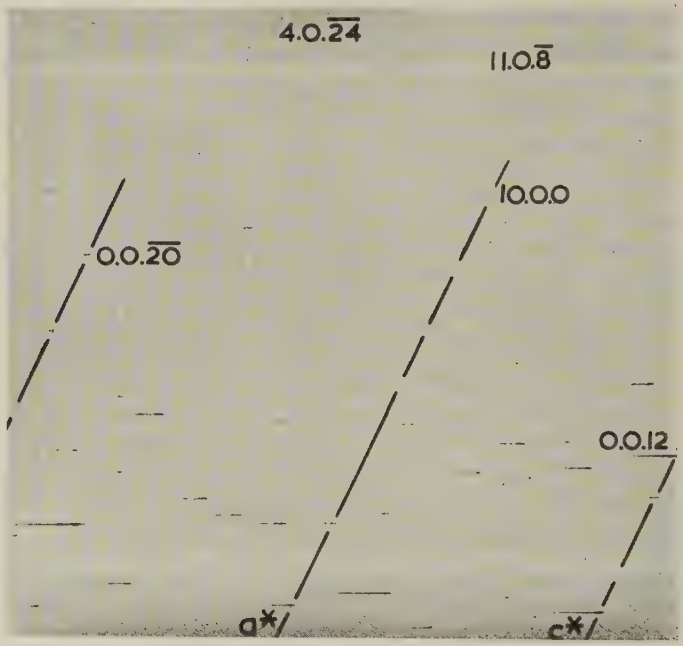


Fig. 1. Zero-layer, normal-beam Weissenberg photograph of pumpellyite from Calumet, Michigan, with the crystal oscillated about the $b$-axis. The streaking of reflections is due to twisting of the crystals about $b$. Cu-$K\alpha$ radiation, Ni filter. Camera diameter 6 cm.

the layer-lines. After careful indexing, it was found that all the anomalous streaks could be satisfactorily accounted for as being due to specified strongly reflecting lattice planes which were in a position to reflect in disoriented parts of the crystal, but not in that part of the crystal responsible for the main maximum in each streak.

From a study of some hundreds of reflections of the form $h0l$, $h1l$, $h2l$, it was found that the condition for reflection from a plane $hkl$ is that $k+l = 2n$. The structure must therefore belong to one of the

space-groups $A2$, $Am$, or $A2/m$. No piezoelectric effect was detected in crystals of pumpellyite from Hicks Ranch, Sonoma County, California, by use of the Giebe and Scheibe tester, and no pyroelectric effect was detected when crystals were placed on aluminium foil and immersed in liquid air. Hence it is likely that the mineral is holosymmetric with the space-group $A2/m$.

## Relation of X-ray cell to morphology.

The best cleavage and the face parallel to which the crystals are flattened is (100) according to the above choice of unit cell. There is a less perfect cleavage parallel to (001). Due to curved growth, the available crystals are quite unsuitable for accurate optical goniometric measurement, and what appear to be single faces are found to give diffuse reflections over a range of as much as 15°. Nevertheless, reflections at approximately 40–45° from (100) are prominent, and some crystals or cleavage fragments give reflections at about 80° from (100). These reflections have been correlated with the faces (102), ($\bar{1}02$), and (001). The face ($\bar{1}01$) has also been recognized. The angles which important faces should make with (100) have been calculated as follows: (102) 39·1°, ($\bar{1}02$) 46·1°, (001) 82·4°, (101) 23·3°, ($\bar{1}01$) 25·9°.

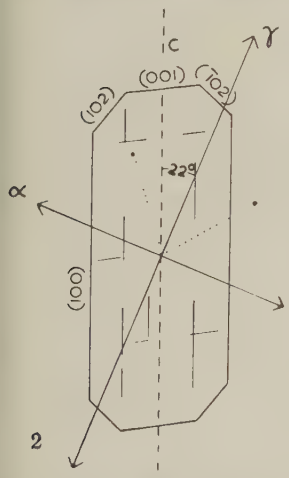


Fig. 2. Optical orientation of pumpellyite from Calumet, Michigan.

The optical orientation is illustrated in fig. 2. In both Calumet pumpellyite and in Californian pumpellyite, $\gamma$ lies in the acute angle between the cleavages. In the former case the extinction angle $\gamma : c$ is about 22° and in the latter case about 4°. The optic axial plane is parallel to (010).

## Twinning.

Pumpellyite may be twinned on (001) as reported by Irving, Vonsen, and Gonyer, and further described below. In addition, twinning sometimes occurs on (100) (fig. 3). Twinning on two planes approximately at right angles to each other has been observed by de Roever (1947a).

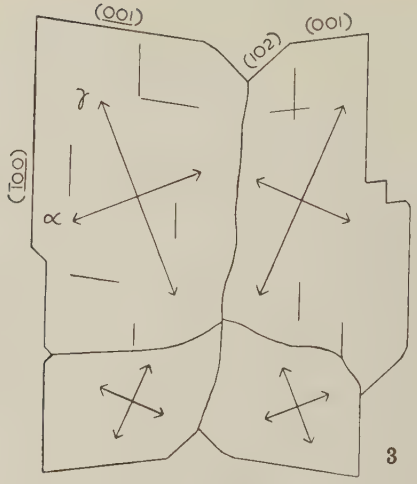


Fig. 3. Cruciform twin of pumpellyite from Calumet, Michigan.

## Related minerals.

Palache and Vassar, Quitzow, also Irving, Vonsen, and Gonyer, have all pointed out similarities between pumpellyite and the epidote minerals. The members of both groups are prismatic in habit with elongation parallel to the symmetry axis, and they have generally similar refractive indices and a tendency towards strong dispersion. Pale varieties of pumpellyite are distinguished from zoisite by inclined extinction in (010) sections, and from both zoisite and clinozoisite by having distinctly lower refractive indices. A characteristic bluish-green $\beta$ absorption tint and positive sign serve to distinguish typical ferriferous pumpellyite from epidote, and the refractive indices and birefringence tend to be lower, although iron-rich pumpellyite (strongly coloured) has higher indices and birefringence than an iron-poor member of the epidote series. Such optically negative pumpellyites as have so far been recognized are brownish in colour, but may be difficult to identify without careful study. The interaxial and intercleavage angle is 82·4° for pumpellyite as against 64° 36′ for epidote. Chemical similarities and differences have been summed up by Irving, Vonsen, and Gonyer in the suggested formulae:

pumpellyite: $Ca_4R_6Si_6O_{23}(OH)_3.2H_2O$, where

$R_6 = (Al,Fe''')_5(Fe'',Mn,Mg)$;

zoisite: $Ca_4Al_6Si_6O_{24}(OH)_2$.

Quitzow (1936) has reported parallel growths of pumpellyite with epidote in rocks from Braunau, Kellerwald, Germany. It is no surprise to find that two cell-edges of pumpellyite, $a$ and $b$, have dimensions similar to those of epidote.

Fig. 4.

Fig. 5.

Figs. 4 and 5. 'Oak-leaf' twinned intergrowths of pumpellyite and lawsonite from Sonoma County, California. In fig. 4, note lamina of lawsonite (in extinction) along the composition plane of the twinned aggregate in (010) section in the lower centre field. Much of this photomicrograph is occupied by sub-prismatic sections of the intergrowths. A cruciform arrangement will be seen in fig. 5 (lower left). Crossed nicols. ×22.

Irving, Vonsen, and Gonyer described twinned crystals of pumpellyite shaped like oak leaves, with the twin plane (001) down the centre. Their locality was Mill Creek, California, where the pumpellyite, an iron-poor variety, was associated with lawsonite. During examination of pumpellyite-lawsonite-glaucophane-rocks from two other Californian localities, Hicks Ranch and Porter Creek, half a mile west of Heldsberg, both in Sonoma County, the present writer has observed similar twins. In most cases there is a thin lamina of intergrown lawsonite along the composition plane, separating the two halves of the twin. Oriented lawsonite also occurs between cusps of pumpellyite (figs. 4 and 5). In these intergrowths $\alpha$ of the lawsonite is parallel to $\beta = b$ of the pumpellyite, and $\beta$ of the lawsonite is parallel to the $a$ crystallographic axis

of pumpellyite, with which $\alpha$ makes a small angle, 12°. This latter fact was confirmed by a special oscillation photograph.

On the basis of the lawsonite cell as described by Wickman (1947), we find a close correspondence between the lengths of the cell-edges along the shared (001) plane. Thus:

$a$ (= $\beta$) of lawsonite, 8·88 kX, is parallel to $a$ of pumpellyite, 8·81 Å.

$b$ (= $\alpha$) ,, 5·75 kX, ,, $b$ (= $\beta$) ,, 5·94 Å.

According to Wickman, the lawsonite structure consists of chains of octahedral groups of O and OH atoms surrounding Al and alined parallel to the $b$-axis and the principal cleavages. The chains are linked by $Si_2O_7$ groups and by calcium atoms. Water molecules occupy the interstices. According to the second hypothesis of Ito (1950), the epidote structure also contains chains of (O,OH) and Al atoms parallel to the $b$-axis, but there are also independent $(Al,Fe)O_6$ octahedra. Linkage is effected both by $Si_2O_7$ and by $SiO_4$ groups. In view of the crystallographic similarities it seems probable that pumpellyite may have a basically similar type of structure to these two minerals. Cell dimensions of epidote, zoisite, lawsonite, pumpellyite, and lombaardite are listed in table I.

Table I. Cell constants of epidote and related minerals.

| | 1. Epidote. | 2. Zoisite. | 3. Lawsonite. | 4. Pumpellyite. | 5. Lombaardite. |
|---|---|---|---|---|---|
| $a$ ... ... | 8·96 Å. | 16·19 Å. | 8·88 kX | 8·81 Å. | 16·10 kX |
| $b$ ... ... | 5·63 | 5·64 | 5·75 | 5·94 | 5·62 |
| $c$ ... ... | 10·20 | 10·13 | 13·30 | 19·14 | 18·20 |
| $\beta$ ... ... | 115° 24′ | 90° | 90° | 97·6° | 115½° |
| | $P2_1/m$ | $Pnma$ | $C222_1$ | $A2/m$ or $A2$, $Am$ | $Pm$, $P2$, or $P2/m$ |

1, Ito, 1947. 2, Ito, 1950. 3, Wickman, 1947. 4, This paper. 5, Nel, Strauss, and Wickman, 1949.

## Powder photograph data.

Powder data are presented in table II for the pumpellyite sample from which the crystal used in the Weissenberg work was selected (Calumet, Houghton Co., Michigan) and for a sample from Hicks Ranch, Sonoma County, California. The photographs used for the measurements were taken with filtered Cu-$K\alpha$ radiation on a 19-cm. camera. Spacings for the Californian mineral show a slight but distinct shrinkage of about 0·1 to 0·2 % relative to those of Calumet pumpellyite. According to fig. 8, the refractive index of this Calumet sample ($\beta$ 1·706)

TABLE II. X-ray powder data for pumpellyite.

(19-cm. diameter camera, Cu-$K\alpha$ radiation, $\lambda = 1{\cdot}5418$ Å. Relative intensities estimated by eye.)

| | Calumet, Michigan. | | Hicks Ranch, California. | |
|---|---|---|---|---|
| *hkl*. | *d* (Å.). | Int. | *d* (Å.). | Int. |
| $10\bar{2}$ | 6·9 | < 1 | 6·8 | < 1 |
| 102 | 6·1 | < 1 | 6·0 | < 1 |
| 004 | 4·75 | 1 | — | — |
| 111 | 4·66 | 1 | 4·67 | 2 |
| 200, $10\bar{4}$ | 4·38 | 2 | 4·39 | 1 |
| $20\bar{2}$ | 4·18 | < 1 | 4·18 | < 1 |
| 104 | 3·96 | < 1 | — | — |
| 202 | 3·79 | 5 | 3·79 | 3 |
| $20\bar{4}$ | 3·45 | 1 | 3·45 | 1 |
| $11\bar{5}$, $10\bar{6}$ | 3·11 | < 1 | 3·11 | < 1 |
| 204 | 3·03 | 2 | 3·03 | 2 |
| 020 | 2·96 | 1 | 2·95 | 1 |
| 115, 300, $30\bar{2}$ | 2·90 | 10 | 2·90 | 10 |
| 022 | — | — | 2·80 | < 1 |
| $20\bar{6}$ | 2·74 | 5 | 2·73 | 5 |
| 302 | 2·69 | < 1 | — | — |
| 311 | 2·64 | 3 | 2·63 | 5 |
| 024 | 2·51 | 2 | 2·51 | 4 |
| $11\bar{7}$, 2.0.10 | 2·452 | 4 | 2·445 | 5 |
| 222 | 2·330 | 2 | 2·325 | 3 |
| | 2·282 | < 1 | 2·282 | 1 |
| $20\bar{8}$ | 2·210 | 3 | 2·205 | 5 |
| $40\bar{2}$ | 2·190 | 2 | | |
| 026 | 2·163 | < 1 | 2·158 | 1 |
| | 2·118 | 1 | 2·112 | 1 |
| $40\bar{4}$ | 2·094 | 1 | 2·088 | < 1 |
| 402 | 2·072 | 1 | 2·069 | 1 |
| | 2·006 | 1 | 2·003 | 2 |
| | 1·920 | 1 | 1·917 | 1 |
| 028 | 1·853 | 1 | 1·847 | 2 |
| | 1·739 | < 1 | 1·739 | < 1 |
| | 1·718 | < 1 | 1·720 | < 1 |
| | 1·698 | 2 | 1·695 | 2 |
| 2.0.10, 1.1.$\bar{11}$ | 1·664 | 2 | 1·661 | 2 |
| | 1·638 | < 1 | 1·636 | < 1 |
| 424 | 1·597 | 3 | 1·594 | 4 |
| 0.0.$\underline{12}$ | 1·581 | 2 | 1·578 | 2 |
| 2.2.$\bar{10}$ | 1·556 | 1 | 1·552 | 3 |
| 408 | 1·513 | 2 | 1·512 | 1 |
| | 1·48–1·49 | 2 | 1·488 | 2 |
| | — | — | 1·476 | 3 |
| | 1·450 | 1 | 1·447 | 2 |
| | 1·414 | < 1 | 1·412 | < 1 |

[*continued on p.* 122

Table II (*cont.*)

| | | | |
|---|---|---|---|
| 1·394 | < 1 | 1·398 | 1 |
| 1·369 | 1 | 1·367 | 1 |
| 1·344 | < 1 | 1·340 | < 1 |
| 1·317 | < 1 | 1·314 | < 1 |
| 1·301 | 1 | 1·299 | 2 |
| 1·263 | < 1 | 1·260 | < 1 |
| 1·249 | 1 | 1·247 | 1 |
| — | — | 1·229 | 1 |
| 1·210 | < 1 | 1·208 | < 1 |
| 1·170 | < 1 | 1·170 | < 1 |
| — | — | 1·113 | < 1 |
| 1·101 | < 1 | 1·099 | < 1 |
| 1·090 | < 1 | 1·089 | < 1 |
| 1·082 | < 1 | 1·079 | < 1 |
| 1·072 | < 1 | 1·070 | < 1 |
| 0·986 | < 1 | 0·985 | < 1 |
| 0·953 | < 1 | 0·953 | < 1 |
| 0·912 | < 1 | 0·911 | < 1 |
| — | — | 0·831 | < 1 |

indicates an iron content of about 8·2 % total iron as $Fe_2O_3$. A partial analysis of the Hicks Ranch mineral showed 3·7 % total iron as $Fe_2O_3$ including 2·7 % FeO, or about 2 % of the theoretical ferric iron end-member. Allowing an average contribution of 3 % FeO as $Fe_2O_3$, calculation shows that the Calumet pumpellyite contains about 12 % of the ferric iron end-member. The observed slight changes in lattice spacings as Fe‴ replaces Al are in the expected direction.

## Chemical composition.

Calculations from the analyses of four pumpellyites (table III), lead to figures closely approximating 56 oxygen atoms (including OH, $H_2O$) per unit cell of 993 cubic Ångströms. Fifty-six oxygen atoms correspond to two formula units as proposed by Irving, Vonsen, and Gonyer (1932), namely: $Ca_4R_6Si_6O_{23}(OH)_3.2H_2O$, where $R$ = Al, Fe, Mg, Mn (and Ti); and (Ti+Al+Fe‴):(Mg+Fe″+Mn) = 5:1. Atomic proportions have therefore been calculated on the basis of 26(O,OH) per half unit cell, any excess or deficiency being placed in the $H_2O$ group. The results show good agreement with Irving's formula. The earlier suggestion of Palache and Vassar (1925), $6CaO.3Al_2O_3.7SiO_2.4H_2O$, can be discarded. Five analyses of synonymous varieties and impure specimens are set out in table IV (p. 124), but only one of these warrants the calculation of a formula.

TABLE III. Chemical analyses of pumpellyite with corresponding atomic proportions.

| | A. | B. | C. | D. |
|---|---|---|---|---|
| $SiO_2$ ... | 37·18 | 38·01 | 37·63 | 37·53 |
| $TiO_2$ ... | — | 0·21 | 0·41 | 0·14 |
| $Al_2O_3$ ... | 23·50 | 25·88 | 27·14 | 25·39 |
| $Fe_2O_3$ ... | 5·29 | 1·11 | — | 1·74 |
| FeO ... | 2·09 | 2·90 | 3·25 | 2·95 |
| MnO ... | 0·13 | 0·17 | 1·03 | 0·13 |
| MgO ... | 3·18 | 1·81 | 1·47 | 2·65 |
| CaO ... | 23·08 | 22·70 | 21·49 | 22·56 |
| $Na_2O$ ... | 0·19 | 0·46 | 0·46 | 0·58 |
| $K_2O$ ... | trace | | 0·08 | nil |
| $H_2O+$ ... | 6·28 | 6·64 | 7·27 | 6·37 |
| $H_2O-$ ... | 0·06 | | 0·12 | 0·09 |
| $P_2O_5$ ... | — | — | — | trace |
| | '100·97' | 99·89 | 100·35 | 100·13 |
| Sp. gr. ... | 3·2 | 3·18 | 3·22 | 3·2 |
| O,OH,$H_2O$ per unit cell as determined for A. | 55·5 | 55·9 | 57·1 | 56·0 |

Atomic proportions on basis of 26(O,OH) per half unit cell.

| | A. | | B. | | C. | | D. | |
|---|---|---|---|---|---|---|---|---|
| Si ... | 5·94 | | 6·07 | | 6·02 | | 6·00 | |
| Ti ... | — | | 0·02 | | 0·05 | | 0·02 | |
| Al ... | 4·42 | 5·06 | 4·88 | 5·03 | 5·12 | 5·17 | 4·78 | 5·01 |
| Fe''' ... | 0·64 | | 0·13 | | — | | 0·21 | |
| Fe'' ... | 0·28 | | 0·39 | | 0·43 | | 0·39 | |
| Mn ... | 0·02 | 1·06 | 0·02 | 0·84 | 0·14 | 0·92 | 0·02 | 1·04 |
| Mg ... | 0·76 | | 0·43 | | 0·35 | | 0·63 | |
| Ca ... | 3·95 | | 3·88 | | 3·68 | | 3·86 | |
| Na ... | 0·06 | 4·01 | 0·14 | 4·02 | 0·14 | 3·84 | 0·18 | 4·04 |
| K ... | — | | — | | 0·02 | | — | |
| OH− ... | 3·00 | | 3·00 | | 3·00 | | 3·00 | |
| $H_2O$ ... | 1·88 | | 2·04 | | 2·44 | | 1·94 | |

A. Calumet, Michigan. Palache and Vassar, 1925. H. E. Vassar, anal.

B. Mill Creek, California. Irving, Vonsen, and Gonyer, 1932. F. A. Gonyer, anal. (pale green pumpellyite).

C. Skaggs, California. Irving, Vonsen, and Gonyer, 1932. F. A. Gonyer, anal. (pale brownish pumpellyite).

D. Asahine, Japan. Tsuboi, 1936. S. Tanaka, anal.

TABLE IV. Inferior analyses of pumpellyite, and analyses of impure material.

| | E. | F. | G. | H. | I. |
|---|---|---|---|---|---|
| $SiO_2$ ... | 37·41 | 36·99 | 35·94 | 39·44 | 42·00 |
| $Al_2O_3$ ... | 24·62 | 25·49 | 19·41 | | 23·05 |
| $Fe_2O_3$ ... | 2·21 | 6·48 | 6·80 | 28·33 | 2·64 |
| FeO ... | 1·81 | — | 4·54 | | 3·74 |
| MnO ... | — | — | — | — | 0·12 |
| MgO ... | 3·46 | — | 2·48 | 3·20 | 1·67 |
| CaO ... | 22·20 | 19·90 | 22·77 | 22·21 | 21·04 |
| $Na_2O$ ... | 0·32 | 3·70 | trace | 0·93 | — |
| $K_2O$ ... | — | 0·40 | — | — | — |
| $H_2O+$ } ... | 7·72 | 7·22 | 8·40 | 6·58 | 5·62 |
| $H_2O-$ } | | | | | 0·12 |
| | 99·75 | 100·18 | 100·34 | 100·69 | 100·00 |
| Sp. gr. | — | 3·180 | 3·11 | 3·229 | (3·2) |

| | | | |
|---|---|---|---|
| Si ... | 6·05 | | |
| Al ... | 4·69 | 4·96 | |
| Fe‴ ... | 0·27 | | |
| Fe″ ... | 0·24 | 1·07 | |
| Mg ... | 0·83 | | |
| Ca ... | 3·84 | 3·94 | |
| Na ... | 0·10 | | |
| OH− ... | 3·00 | | |
| $H_2O$ ... | 2·61 | | |

E. *Chlorastrolite*, Isle Royale, Michigan. Hawes, 1875. G. W. Hawes, 1900, anal.

F. *Chlorastrolite*, Isle Royale, Michigan. Whitney, 1847. J. D. Whitney, anal.

G. *Zonochlorite*, Neepigon Bay, Lake Superior. Hawes, 1875. G. W. Hawes, anal.

H. *Lotrite*, Lotru Valley, Carpathians. G. Munteanu-Murgoci, 1900, anal.

I. Impure pumpellyite, Levikha, Ural Mountains. 'Corrected' by Kvasha to allow for quartz and sphene. Epidote is also present. The correction for quartz is plainly insufficient. $\beta$ 1·697–1·702; $\gamma-\alpha$ 0·012; $2V_\gamma$ (blue) 51°, $2V_\gamma$ (red) 35°. Kvasha, 1950. T. L. Pokrovska, anal.

## THERMAL ANALYSIS.

Preliminary dehydration experiments on pumpellyite from Asahine, Japan, were carried out by Tsuboi (1936). A differential thermal analysis of Asahine pumpellyite by Dr. R. J. McLaughlin (fig. 6) shows no significant reaction until temperatures are reached of 740° and 810° C., where there are two strong overlapping endothermic peaks, followed by an exothermic peak at 910°. This evidence supports the suggested formula to the extent that it indicates two types of water bonding. The water is lost at a rather higher temperature than in the case of lawsonite, for which Dr. McLaughlin found endothermic peaks at 630° and 760°. Corresponding figures due to Norin (1942) are 675° and 805°. Kvasha (1950) found endothermic peaks for pumpellyite at about 700° and 800° followed by an exothermic peak at 850°.

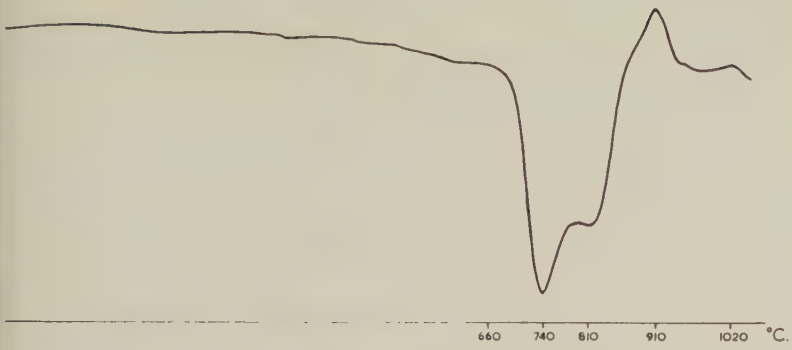


FIG. 6. Differential thermal analysis curve for pumpellyite.

## OPTICAL STUDY

Due to the tendency for crystals to lie flat on (100) it is almost impossible to make satisfactory measurements of the $\alpha$ and $\gamma$ indices on powders. Hence, wherever possible, indices have been determined on single crystals mounted on the stage goniometer with the $b$ ($= \beta$) axis parallel to the axis of rotation. With this arrangement, the optic axial angle as well as all three indices can be measured on the same part of a single grain. For accurate results it is usually essential to use very narrow splinters in order to minimize the effects of zoning and distorted crystal growth. Under favourable conditions the accuracy actually obtained is estimated as $\pm 0{\cdot}001$ for indices and $\pm 2°$ for 2V ($Na_D$ light). Under less favourable conditions these errors may be more than doubled. The refractive index $\beta$ can be determined fairly satisfactorily on loose crystals too small to be mounted on the stage goniometer. Due to the strong dispersion of the optic axes, sections parallel to the length of the crystals show anomalous interference tints, brownish for sections containing $\beta$ and $\gamma$, and bluish for sections containing $\alpha$ and $\beta$. Significant data are listed below, all measurements being for $Na_D$ light.

*Calumet, Michigan* (B.M. 1926,226, used for unit-cell determination).—Dark lustrous green crystals showing distinct zoning. Indices averaged from six crystals are considered representative of the sample as a whole.

| | Average. | Extremes. | Pleochroism. |
|---|---|---|---|
| $\alpha$ ... | 1·698 | 1·695–1·702 | almost colourless |
| $\beta$ ... | 1·706 | 1·703–1·709 | deep bluish-green |
| $\gamma$ ... | 1·720 | 1·717–1·722 | almost colourless |
| $\gamma-\alpha$ ... | 0·022 | — | — |
| $2V_\gamma$ ... | 80° | 75°–85° | |

Dispersion $r < v$ strong. $\gamma : c$ (in acute angle $\beta$) = 20–25°.

The birefringence, 0·022, agrees fairly closely with the figures of 0·018–0·020 reported by Burbank (1927), Korzhinsky (1944), and Zavaritsky (1944) for comparable deeply coloured pumpellyites.

*Calumet, Michigan* (H 90919).—This material, a specimen of which has been provided by Professor C. Frondel, is that from which Palache and Vassar's original analysis sample was selected. Most of the crystals are strongly zoned and great variation in colour is apparent from very pale to very dark bluish-green or even slightly brownish bottle-green. The darker regions have higher indices than the lighter, stronger dispersion, and larger optic axial angles. In zoned crystals, dark-green zones usually surround lighter cores. Data for two representative zoned crystals are given below, and data for other crystals from the same sample are incorporated in fig. 9 (p. 131).

| | Crystal no. 1. | Crystal no. 2. |
|---|---|---|
| $\alpha$ ... | 1·676–1·678 | 1·687–1·698 |
| $\beta$ ... | 1·677–1·679 | 1·691–1·707 |
| $\gamma$ ... | 1·690–1·693 | 1·706–1·720 |
| $\gamma-\alpha$ ... | 0·014–0·015 | 0·019–0·022 |
| $2V_\gamma$ ... | 29°–33° | 57°–76° |
| Dispersion | $r < v$ distinct | $r < v$ very strong |

In one small aggregate of pumpellyite needles from this specimen, it was found that although $\beta$ varied from 1·694 to 1·710, for the majority of grains it varied within narrow limits, 1·701–1·702, which gives a fair average for the particular small aggregate as a whole. After crushing and centrifuging in bromoform to separate any felspar and quartz, total iron was estimated as $Fe_2O_3$ by the *o*-phenanthroline colorimetric method, with the result 7·6 % $Fe_2O_3$, including 2·1 % FeO. This compares closely with Palache and Vassar's figures of 5·29 % $Fe_2O_3$ + 2·09 % FeO (7·61 % total iron as $Fe_2O_3$). Two less homogeneous hand-picked dark-green samples with an estimated average $\beta$ of 1·700, treated in the same way, gave 7·0 % and 7·1 % of total iron as $Fe_2O_3$. The iron-poor nature of the almost colourless Calumet pumpellyite was confirmed in a qualitative way by a colorimetric determination of 3·4 % total iron oxides on a small, impure, and rather strongly zoned sample.

*Hicks Ranch, Sonoma County, California.*—Veins of light green pumpellyite traverse pumpellyite-lawsonite-glaucophane-rock. Pumpellyite occurs in the veins as needles several millimetres long flattened on (100). Colorimetric determinations showed 2·7 % FeO, 0·7 % $Fe_2O_3$ (3·7 % total iron as $Fe_2O_3$), and 0·26 % MnO. The optical properties

correspond closely with those given by Irving, Vonsen, and Gonyer (1932) for iron-poor Californian pumpellyite

| | Hicks Ranch. | Mill Creek (Irving et al. 1932). | Pleochroism. |
|---|---|---|---|
| $\alpha$ ... | 1·681 | 1·679 | colourless |
| $\beta$ ... | 1·682 | 1·680 | very pale green |
| $\gamma$ ... | 1·695 | 1·692 | colourless |
| $\gamma-\alpha$ ... | 0·014 | 0·013 | |
| $2V_\gamma$ ... | 39° | 40° | |
| $\alpha:(001)$ ... | 12° | 12° | |
| Dispersion | $r < v$ (distinct) | $r < v$ | |

Thin sections from Hicks Ranch show the twinned pumpellyite-lawsonite intergrowths already referred to (figs. 4, 5). The extinction

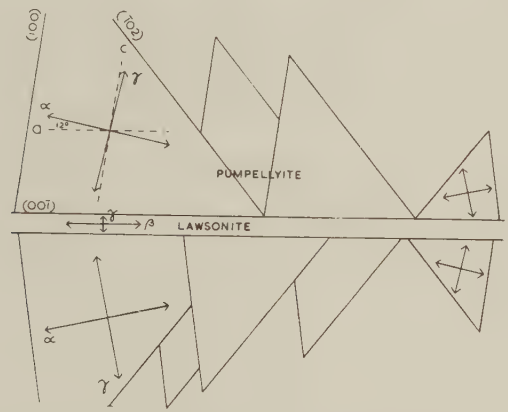


Fig. 7. Pumpellyite twinned on {001}, with intergrown lawsonite, shown in diagrammatic section parallel to {010}. Sonoma County, California.

angle between $\alpha$ and the twin plane (001) in adjacent parts of twins is 12° as reported by Irving and collaborators. An interpretation of the cuspate 'oak leaf' twins is illustrated in fig. 7. The cusps appear to be due to a combination of (100) and ($\bar{1}02$) faces which theoretically make an angle of 46° with each other. According to an alternative explanation they might be due to (100) and ($\bar{1}0\bar{2}$) at an angle of 39°. Actual measurements of the cusp angle on the universal stage were usually 40–45°. The extinction angle between $\gamma$ and the face making a large angle with (001) was consistently found to be close to 7°. If the face is (100), the extinction angle $\gamma$:(100) should be $4\frac{1}{2}$° according to the

figured interpretation, but 19½° according to the alternative explanation. This supports fig. 7, although the agreement is not perfect. The anomalies are considered to be due partly to difficulties of measurement and partly to disorientation of various parts of the aggregates, and perhaps to vicinal faces making small angles with (100) and ($\bar{1}$02).

*Asahine, Titibu-gôri, Saitama prefecture, Japan.*—A large hand-specimen was provided by Professor Tsuboi, who described the material in 1936 (analysis D, table III). Bladed crystals of pumpellyite, 1 cm. or more long, make up veins cutting metagabbro, itself rich in pumpellyite. Thin sections show that the large pumpellyite 'crystals' are closely twinned and slightly disoriented aggregates. 'Oak leaf' twinning is sometimes developed. Very slight variation was observed in optical properties, $\beta$ ranging from 1·687 to 1·690. Typical refractive index figures agree closely with those of Tsuboi, but significant discrepancies were found in the optic axial angle, and in the extinction angle which was measured on twinned crystals. The revised values only have been utilized in the graphs showing the relation between optical properties and chemical composition (figs. 8, 9, p. 131).

| | | Revised values. | Data due to Tsuboi (1936) |
|---|---|---|---|
| $\alpha$ | ... | 1·686 | 1·686 |
| $\beta$ | ... | 1·688 | 1·690 |
| $\gamma$ | ... | 1·699 | 1·698 |
| $\gamma-\alpha$ | ... | 0·013 | 0·012 |
| $2V_\gamma$ | ... | 49½° | 36–40° |
| $\alpha$:(001) | ... | 15½° | 11–12° |

*Howell's Point, Riverton, Southland, New Zealand.*—This material was collected by Professor C. E. Tilley. Small prismatic deep bluish-green crystals occur embedded in chlorite in albite-filled amygdales in a spilitic pillow lava. The crystals are dominated by the faces (100), ($\bar{1}$01), and ($\bar{1}$02). The optical properties were found to be remarkably uniform:

| | | | |
|---|---|---|---|
| $\alpha$ | ... | 1·694 | colourless |
| $\beta$ | ... | 1·698 | deep bluish-green |
| $\gamma$ | ... | 1·713 | colourless |
| $\gamma-\alpha$ | ... | 0·019 | |
| $2V_\gamma$ | ... | 65° | |

Extinction angle $\gamma:c = 17°$ in acute angle $\beta$.

*North Range, Taringatura survey district, Southland, New Zealand.*—Pumpellyite is occasionally present as a reconstituted mineral in the greywackes of the district, and also as a constituent of metasomatic bodies of quartz, albite, adularia, and pumpellyite which locally replace

laumontitized vitric tuffs. It occurs as aggregates of tiny prismatic crystals less than 0·05 mm. long and of rhombic cross-section due to the dominance of (100) and (001) faces. In a typical specimen the optic axial plane is parallel to (010) as in all the pumpellyites described above, $\gamma$:$c$ is approximately 27°, $\beta$ 1·70–1·72, $2V_\gamma$ is large, dispersion strong with $r < v$, and there is normal pleochroism $\alpha = \gamma =$ almost colourless, $\beta =$ bluish-green to yellowish-green. Such properties are those of ordinary, moderately iron-rich pumpellyite. In some cases a transition was observed from greenish to brownish absorption tints. A golden-brown, pleochroic mineral in a metasomatic rock (O.U. 8811) of negative sign and unusually high refractive indices and birefringence was also proved to be pumpellyite, a powder photograph showing a pattern indistinguishable from that of Calumet pumpellyite. Unfortunately this interesting material was much too fine-grained and poorly crystalline to allow detailed measurement of optical properties. Nevertheless two distinct optical orientations were observed, as follows:

(i) Optic axial plane parallel to (010); $\beta$ 1·71–1·73; $\gamma - \alpha = 0{\cdot}02$; $2V_\alpha$ variable, 80–20°; dispersion $r > v$ strong; pleochroic with $\alpha = \gamma$ = very pale bluish-green to brownish-green, $\beta =$ pale to deep golden-yellow.

(ii) Optic axial plane perpendicular to (010) with $\gamma$ parallel to the length of the fibre; $\gamma$ variable, up to 1·75; $\gamma - \alpha$ estimated on thin sections with Berek compensator as about 0·028; $2V_\alpha$ variable from almost uniaxial to 60°; dispersion $r < v$ strong; pleochroic with $\alpha = \beta =$ pale bluish-green to pale brownish-green, $\gamma =$ golden-yellow to yellow-brown.

It is likely that there is a continuous series between orientations (i) and (ii) with virtually uniaxial intermediate varieties.

Irving, Vonsen, and Gonyer (1932) have shown that the brownish-yellow absorption tint for iron-poor pumpellyite from Skaggs, California, can be correlated with the presence of 1·03 % MnO, but in other respects the optical properties of the Skaggs mineral are normal. Quitzow (1936) has described pumpellyite from Braunau, Kellerwald, having all transitions from the normal green variety of positive sign, $r < v$, to material having negative sign and very small optic axial angle, $r > v$, and the pleochroic scheme $\alpha = \gamma =$ faintly brownish, $\beta =$ yellowish-brown (parallel to the length of the fibres). The double refraction of the brown variety is greater than that of the green. These properties are comparable with those of the North Range pumpellyite no. 8811, orientation (i). Lacroix (1942) has also described transitions from green to

brown varieties. Quitzow suggested that the brown colour of his material, like that of Irving and collaborators, might be due to the presence of manganese. This can, however, hardly be the explanation of the anomalous properties of the North Range pumpellyite. The rock 8811 was estimated to contain 8 % pumpellyite, and a partial analysis revealed the presence of 0·025 % MnO. Hence even assuming that all the MnO is contained in the pumpellyite, the mineral can hardly contain more than the order of 0·3 % MnO. On the other hand, the high indices and birefringence suggest high iron.

## Relation of optical properties to chemical composition.

The systematic nature of the variations of the optical properties of pumpellyite has been pointed out by de Roever (1947b). In eastern Borneo, he found a continuous series from colourless varieties with low refractive index (1·67), low birefringence (0·010), small $2V_\gamma$, and feeble dispersion, to dark-green varieties with high refractive index (1·72), higher birefringence (0·018), large $2V_\gamma$, and strong dispersion. All these conclusions are confirmed in the present study and they are correlated with varying iron content. Furthermore, it appears that the increase in $2V_\gamma$ with refractive index can be continued to values greater than 90° when the sign becomes negative ($\beta$ 1·72–1·73). It is probable that the optic axial plane changes from parallel to (010) to perpendicular to (010) as the refractive index for vibrations parallel to the *b*-axis, which is normally $\beta$, continues to increase at a greater rate than those in (010) and eventually exceeds them for values of about 1·74 to 1·75. An explanation of the properties of the yellow-brown Taringatura pumpellyite would thus be afforded, but until analysable material is found with these properties, the question cannot be decided satisfactorily. The suggested explanation is shown diagrammatically in fig. 8 as an extrapolation of the refractive index curves for more normal pumpellyites, based on four published analyses and four new partial analyses. Many measurements on single crystals show a close correlation between optic axial angle and refractive index, and this is shown in fig. 9.

*Extinction angles.*—The measurement of extinction angles in (010) sections of pumpellyite is usually a matter of some difficulty, and measurements are probably not very reliable except where made on twinned crystals. The limited data available indicate an increase in extinction angle with increasing iron content (fig. 9).

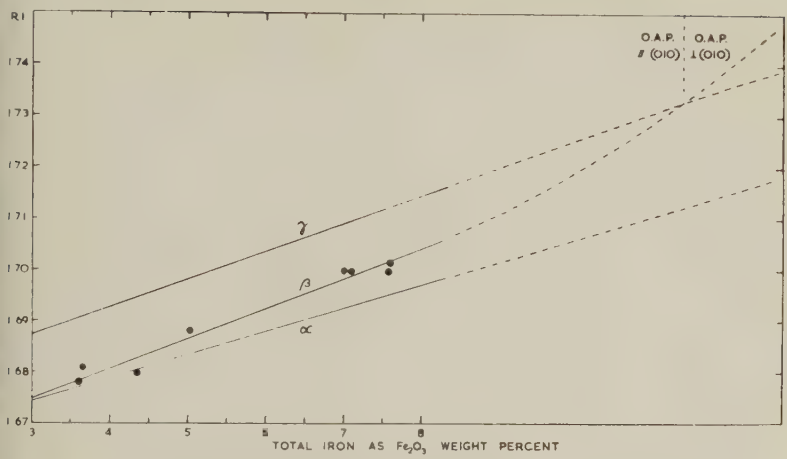


FIG. 8. Refractive indices of pumpellyite related to iron content. Points represent data from published analyses and new partial analyses, $\beta$ alone being plotted. Dashes—probable form of refractive index curves beyond the analysed range.

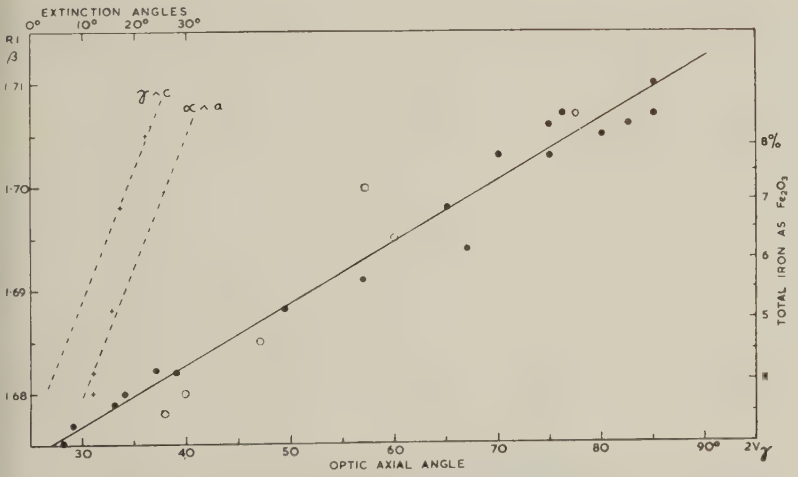


FIG. 9. Variation of 2V and extinction angles of pumpellyite with refractive index and hence with iron content. Points—optic axial angle and $\beta$ index determined on single crystals on the stage goniometer. Circles—optic axial angle data from the literature. Crosses—extinction angles.

### Synonymous varieties.

In 1847 Whitney described under the name *chlorastrolite*, small rounded pebbles from the shore of Isle Royale, Lake Superior, consisting of a finely radiating, light bluish-green material. Hawes (1875) showed that this was not a homogeneous mineral, and on the basis of his analysis (table IV, E) he ascribed it to impure prehnite. Owing to the variable sign of elongation, Lacroix (1887) considered the material to be a supposed pleochroic variety of thomsonite. Professor C. Frondel has kindly pointed out that the green mineral is pumpellyite and he has provided several small pebbles. An X-ray powder photograph proves to be indistinguishable from photographs of type pumpellyite, and so confirms the identification. The refractive index $\beta$ is 1·675–1·682. Hawes's analysis is seen to be in excellent agreement with pumpellyite analyses. In the pebbles examined by the writer, the pumpellyite is associated with some chalcedony and albite. In 1873 Foote described a massive mineral banded in different shades of green as a new species *zonochlorite*. It occurs both as shore pebbles and in situ in amygdaloidal trap at Neepigon Bay, Lake Superior. Hawes (1875) analysed it (table IV, G) and concluded that it was impure 'chlorastrolite'.

According to Kvasha (1950), Sobolev (1947) has shown that *lotrite* (Munteanu-Murgoci, 1900, 1901) is the same as pumpellyite. Sobolev's paper has not been seen by the present writer, but optical examination of material from the type locality (Lotru valley, southern Carpathians) kindly provided by the British Museum, shows that Sobolev's determination is undoubtedly correct. A single grain was mounted on the stage-goniometer and the following properties were determined:

| New data. | | | Data due to Murgoci (1900) | | |
|---|---|---|---|---|---|
| $\alpha$ | ... | 1·674 | $n$ | ... | 1·67 |
| $\beta$ | ... | 1·675 | $\gamma-\alpha$ | ... | 0·014 |
| $\gamma$ | ... | 1·689 | $2E_\gamma$ | ... | 30° |
| $\gamma-\alpha$ | ... | 0·015 | 2V | ... | 18° |
| $2V_\gamma$ | ... | 28° | $\beta$ parallel to length | | |
| $\beta$ parallel to length | | | Extinction angle to cleavage = 28° | | |
| Dispersion $v < r$ moderate | | | | | |

Murgoci's analysis (table IV, H) agrees reasonably well with pumpellyite. His extinction angle seems rather high for a pumpellyite with about 3 % total iron oxides as is indicated by the other optical properties, but as this is a difficult measurement to make on such poorly crystalline material, this is not a serious discrepancy. As Murgoci's description

and chemical analysis were both reasonably adequate, it is unfortunate that his work should have been overlooked. The name 'pumpellyite' is now firmly entrenched in the literature and 'lotrite' must lapse into synonymy, in spite of priority.

*Acknowledgements.*—The above work was carried out at the Department of Mineralogy and Petrology, Cambridge. The writer wishes to express his keen appreciation of the encouragement and suggestions received from Professor C. E. Tilley and Drs. N. F. M. Henry, S. R. Nockolds, and W. A. Wooster, and for the thermal analysis carried out by Dr. R. W. McLaughlin. Mr. K. Rickson has given technical assistance with the photomicrographs and X-ray powder work. Comparative material has been received from Professors C. Frondel, N. E. Odell, and S. Tsuboi, from Dr. J. E. de Villiers (lombaardite), and from the British Museum (Natural History). The writer thanks sincerely all those concerned.

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# *An occurrence of harmotome in north-west Ross-shire.*

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[Communicated by Dr. W. Campbell Smith; taken as read November, 1952.]

THE minerals to be described were found by Dr. Duncan M. Morison, of Edinburgh, and the writer in a small quarry having a national grid reference of 29/076184, which is at present being excavated for road surfacing material. The quarry is situated on the east side of the coast road between Lochinver and Ullapool at a point $\frac{1}{4}$ mile south-west of the southern margin of Loch an Arbhair (called Loch a' Choin on early editions of the Ordnance Survey sheet 101) and $\frac{3}{4}$ mile south-west of the bridge carrying the Lochinver–Ullapool road over the river Kirkaig, the course of which here marks the boundary between the counties of Sutherland and Ross.

The quarry has been excavated along the outcrop of a fault, having a NE.–SW. strike, within the Lewisian of the foreland area which is here made up of felspathic and hornblendic gneisses. Within the quarry gneiss, undisturbed by faulting, is exposed, but the principal rock type is a slickensided and mineralized fault breccia. The rock outcropping at the north-eastern margin of the brecciated zone might be termed a concussion breccia, the angular and broken fragments having moved so little in relation to one another that the position which they must have occupied in the country-rock before it was fragmented may still be easily discerned. Towards the centre of the breccia, where mineralization is heaviest, movement has taken place, and fragments of several rock types may be found in a single hand-specimen. The outcrop of the fault breccia appears to be limited to the confines of the quarry.

The most abundant mineral forming the binding material of the breccia is haematite, which is largely earthy and amorphous; in cavities and fissures, however, it has developed characteristic mamillated surfaces. Calcite is fairly abundant as a vein-stuff and in cavities has developed prismatic crystals of 'nail-head' variety. Crystalline baryte occurs in veins through the breccia, and in cracks and cavities assumes the cockscomb habit. It is commonly reddish in colour, due probably to iron staining, and minute haematite crystals developed on the cockscomb surfaces may mask the true form and colour.

Small and unweathered harmotome crystals are found coating the vein-stuff in cracks and cavities throughout the breccia, although these occurrences are not abundant. The crystals (S.M.C. 442/36–43)[1] which are found emplanted on the vein-stuff are unweathered, water-clear, colourless, and lustrous, the largest examples being some 6 millimetres in length, although most of the crystals are little more than half that size.

All the harmotome crystals exhibit characteristic cruciform penetration twinning. Crystal faces observed are (100), (110), (010), and (001). The appearance of the crystals varies slightly depending on the relative development of the faces; typically, however, the (100) face is much better developed than (110) which is usually small, and the re-entrant angle (001) is poorly developed. Striations were seen on the (100) faces parallel to the edge between (100) and (010) and that between (100) and (001); and on the (010) face parallel to the edges between the (010) face and the bounding (110) faces, the striae meeting on the central line and so forming a herring-bone pattern.

Specific gravity 2·44. Refractive indices: $\alpha$ 1·508, $\gamma$ 1·514, $\gamma-\alpha$ 0·006 (Na).

In 1888 A. M. Lévy and A. Lacroix[2] determined the refractive indices of a harmotome crystal from Strontian, Argyllshire, as $\alpha$ 1·503, $\beta$ 1·506(?), $\gamma$ 1·508; values which appear to have been accepted by most later workers. Since the indices determined for the Ross-shire specimens were at variance with the findings of Lévy and Lacroix it was thought desirable to redetermine the refractive indices of crystals from the better known Scottish localities. Specimens were therefore examined from the Strontian area (Corrantee, Middleshope, Whitesmith, Bellsgrove, and Fee Donald or Feith Dhomhail) and from Bowling, Dumbartonshire, and it was found that, with little variation, the indices were in agreement with those of the Ross-shire specimens $\alpha$ 1·508, $\gamma$ 1·514. It is of interest to recall here, however, that the refractive indices determined for harmotome from Glen Riddle, Delaware Co., Pennsylvania, were[3] $\alpha$ 1·506, $\beta$ 1·509, $\gamma$ 1·514.

X-ray powder photographs obtained from small fragments of the Ross-shire specimens, and examples from Whitesmith, Strontian (S.M.C. 442/16); Bowling, Dumbartonshire (S.M.C. 442/10); and Glen Arbuck, Dumbartonshire (S.M.C. 442/18) are identical and appear to be in fair

[1] Numbers in parentheses refer to registered numbers in the Scottish Mineral Collection of the Roya lScottish Museum.

[2] A. M. Lévy and A. Lacroix, Les minéraux des roches. Paris, 1888. p. 309.

[3] A. E. Meier, Amer. Min., 1939, vol. 24, p. 555. [M.A. 8–298.]

agreement with the spacings in Ångström units for harmotome from Uganda published by Bannister and Hey (table I).

TABLE I. X-ray powder data for harmotome from Ross-shire and Uganda.

| Ross-shire.[1] | | Bannister and Hey.[2] | | Ross-shire.[1] | | Bannister and Hey.[2] | |
|---|---|---|---|---|---|---|---|
| *d.* | Int. | *d.* | Int. | *d.* | Int. | *d.* | Int. |
| 8·24 Å. | s | 8·11 Å. | s | 2·13 Å. | m | 2·16 Å. | m |
| 7·17 | s | 7·16 | s | 2·04 | m | 2·03 | w |
| 6·26 | s | 6·25 | s | 1·94 | s | 1·95 | m |
| 4·94 | m | 4·96 | m | 1·88 | vw | 1·91 | vw |
| 4·26 | w | — | — | 1·82 } b | w | 1·84 | w |
| 4·03 | s | 4·07 | s | 1·80 } | | 1·80 | w |
| 3·87 | mw | 3·50 | m | 1·75 | mw | 1·74 | w |
| 3·20 | s | 3·18 | s | 1·72 } b | ms | 1·72 | ms |
| 3·06 | s | — | — | 1·69 } | | 1·68 | w |
| 2·88 | mw | 2·93 | w | 1·52 | m | 1·54 | m |
| 2·71 | s | 2·69 | s | 1·47 | w | 1·48 | m |
| 2·62 | s | — | — | 1·43 | vw | — | — |
| 2·51 | m | 2·52 | m | 1·36 | w | 1·37 | w |
| 2·45 | vw | — | — | 1·32 | w | 1·33 | w |
| 2·35 | m | 2·34 | m | | | 1·26 | w |
| 2·29 | m | — | — | | | 1·17 | vw |
| 2·23 | w | 2·25 | w | | | | |

*Acknowledgements.*—The writer is grateful to Professor W. Q. Kennedy for permission to have the X-ray powder photographs taken at the Geological Department of Leeds University and to Mr. A. K. Temple for taking the photographs. Thanks are also due to Mr. J. A. Boyd of Inverkirkaig for his help in the field.

[1] University of Leeds, Department of Geology, Film number P.2988.

[2] F. A. Bannister and M. H. Hey, Min. Mag., 1942, vol. 26, p. 224.

# *A hydrous mica from Yorkshire fireclay.*

By K. Carr, B.Sc., R. W. Grimshaw, B.Sc., Ph.D., A.R.I.C., and A. L. Roberts, Ph.D., F.R.I.C.

Fuel Department, University of Leeds

[Taken as read January 22, 1953.]

RECENT investigations[1] into the mineralogical constitution of fireclays have revealed the presence of a micaceous mineral in all samples examined. Naturally-occurring clays may contain up to 30 % of this type of mineral, and exceptional concentrations have been found in the Yorkshire area. Tests on the purified mineral from this source have proved it to be a hydrous mica of an unusually large grain-size.

## *Method of separation.*

Although a mica-type mineral has long been known as a constituent of most fireclays, the isolation of the pure mineral species has proved difficult. Samples have been isolated from only three clays, from the outcrop and drift mine workings of the Better Bed clay, near Leeds. A clay from an outcrop at Tong (G.M. Ref. $^{42}36^{43}15$ Sheet 77) was obviously rich in large particles of mica and it is from this source that the purest sample has been secured.

The clay was thoroughly dispersed in water with vigorous stirring. The suspension was then poured through a nest of sieves; the largest of which had apertures of 251 $\mu$ and the smallest apertures of 66 $\mu$. Each fraction was washed until free from adhering smaller particles.

There was obviously a concentration of mica flakes in the sample retained on the large aperture sieves, but admixed were sand and coal grains, and some undispersed clay. Further separation was achieved by rolling the mixture down a vibrating inclined ebonite board. The flat micaceous plates adhered, whilst the rounded quartz and coal particles rolled away. The final traces of impurity were removed by heavy liquid separation. It was only possible to separate about five grams of pure mineral from two kilograms of clay.

The above method was excellent for isolating mica particles of about

[1] K. Carr, R. W. Grimshaw, and A. L. Roberts, Trans. Brit. Ceramic Soc., 1952, vol. 51, p. 334.

100$\mu$, below this size heavy liquid separation was more effective, although really pure samples were difficult to obtain. The large-particled mica flakes were free from any quartz or coal contamination, and were silvery white in colour.

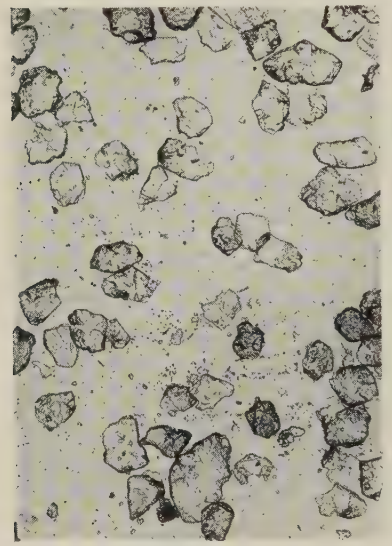

Fig. 1.

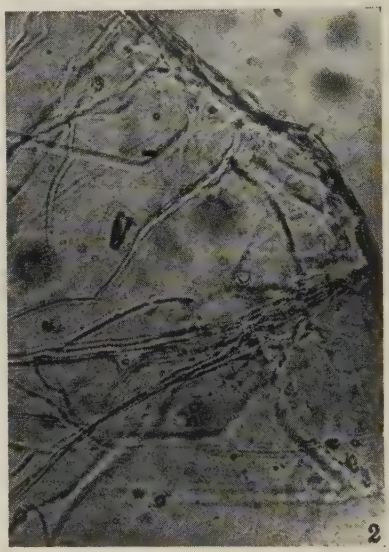

Fig. 2.

Figs. 1 and 2. Photomicrographs of micaceous flakes from fireclay. Fig. 1, $\times 5$; fig. 2, $\times 300$, showing fissures.

*Properties of micaceous mineral.*

*Optical.*—The mineral appeared to be typical of the mica family when observed under the microscope. Some of the flakes were hexagonal in shape, and cleavage was parallel to the basal section (fig. 1). Under high magnification, cracks could be seen in most of the plates, particularly at the crystal boundaries (fig. 2). Along these fissures were traces of an alteration mineral which absorbed the dyes suffranine and malachite-green, suggesting colloidal or clay material.

A negative biaxial interference figure was obtained on the large flakes, but it was not as distinct as would be expected from muscovite. This may be due to the degree of alteration. The 2V angle was small, being between 5° and 10°. The birefringence was low, and the refractive index 1·578. These optical data agree well with those of other hydrous

micas or illites described in the literature.[1] The mica had a specific gravity of 2·913.

*Chemical analysis.*

Standard methods of silicate analysis were used. The results are shown in table I.

TABLE I. Chemical analyses.

| | Micaceous mineral. | Muscovite (Jacob[2]). |
|---|---|---|
| $SiO_2$ ... ... | 46·75 | 44·85 |
| $TiO_2$ ... ... | 1·15 | trace |
| $Al_2O_3$ ... ... | 32·43 | 36·95 |
| $Fe_2O_3$ ... ... | 2·98 | 1·54 |
| FeO ... ... | n.d. | 1·36 |
| MgO ... ... | 1·00 | 0·00 |
| CaO ... ... | 1·04 | 0·00 |
| $Na_2O$ ... ... | 0·94 | 1·78 |
| $K_2O$ ... ... | 5·72 | 9·13 |
| $H_2O+$ ... ... | 8·01 | 4·08 |
| $H_2O-$ ... ... | 0·04 | 0·00 |
| | 100·06 | 99·69 |
| $SiO_2/R_2O_3$ molecular ratio ... ... | 2·31 | 1·91 |
| Molecular proportion of alkali ... ... | 0·76 | 1·25 |

The $SiO_2/R_2O_3$ ratio of 2·31:1 is greater than that for ideal mica of 2:1. The loss on ignition is considerably higher than that of muscovite, whilst the alkali content is not as great.

*Differential thermal analysis.*

The characteristic thermal curve given by the micaceous mineral is shown in fig. 3, along with a curve for muscovite mica. A comparison record of the original Tong clay is also shown. There are three well-defined endothermic peaks, observed in all tests on the purified mineral, none of which are shown in the thermal curves of micas of the muscovite or biotite type. The first peak at 570° C. may be caused by the alteration product, which cannot be removed entirely, although its magnitude can be influenced by the degree of purification. The other two endo-

[1] R. E. Grim, R. H. Bray, and W. F. Bradley, Amer. Min., 1937, vol. 22, p. 813. [M.A. 7–12]. G. Nagelschmidt and D. Hicks, Min. Mag., 1943, vol. 26, p. 297. E. Maegdefrau and U. Hofmann, Zeits. Krist., 1937, vol. 98, p. 31; Sprechsaal, 1941, vol. 74, p. 369. T. F. Bates, Amer. Min., 1947, vol. 32, p. 625 [M.A. **10**–365].

[2] J. Jakob, Zeits. Krist., 1925, vol. 62, p. 443 [M.A. **3**–81].

thermic effects at 625° C. and 660° C. are probably characteristic of the mineral.

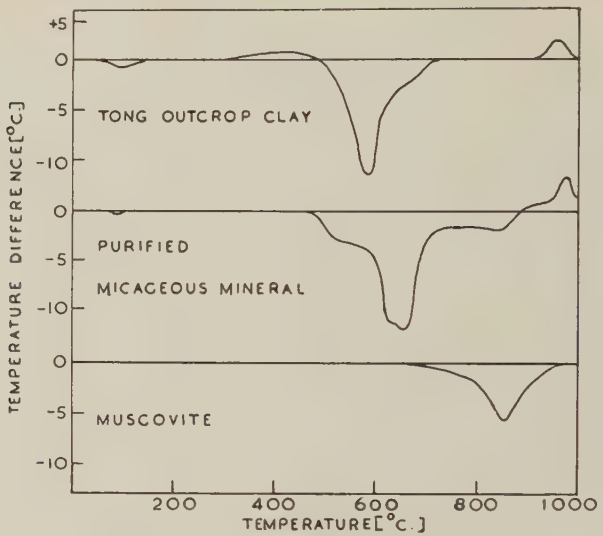


FIG. 3. Differential thermal analysis curves.

*X-ray analysis.*

Powder photographs of the micaceous mineral give spacings as shown in table II. Also shown are the spacings for muscovite and kaolinite. The lines are in agreement with those of Nagelschmidt, Grim, and others for hydrous mica, except for the additional lines at 7·18 and 3·57 Å., which are possibly due to a kaolin alteration mineral. On heating to 500° C., the 10 Å. line is unchanged in sharpness or position. Furthermore the 060 line is at 1·50, thus indicating a micaceous mineral of the dioctahedral series. Single crystal photographs have been taken, but the complete analysis has not yet been accomplished.

*Structure of the mineral.*

The mineral is of the micaceous type, but with a higher $SiO_2/R_2O_3$ ratio, less alkali, and more lattice-held water than true muscovite. Similar minerals have been described by Grim et al., Nagelschmidt, Maegdefrau and Hofmann, Bates, and by Brammall, Leech, and Bannister,[1] and ascribed the name 'illite' or 'hydrous mica'. No previous author, however, has been able to isolate the mineral in such

[1] A. Brammall, J. G. C. Leech, and F. A. Bannister, Min. Mag., 1937, vol. 24, p. 507.

TABLE II. X-ray spacings.

| Micaceous mineral. | | Muscovite. | | Kaolinite. | |
|---|---|---|---|---|---|
| *d* (Å.). | Int. | *d* (Å.). | Int. | *d* (Å.). | Int. |
| 9·98 | s | 10·16 | s | — | — |
| 7·18 | vs | 4·98 | s | 7·14 | vs |
| 4·97 | w | 4·49 | s | 4·46 | vs |
| 4·44 | w | 4·31 | vw | 4·17 | s |
| 4·09 | vw | 4·17 | vw | 3·86 | m |
| 3·83 | vw | 3·92 | w | 3·58 | vs |
| 3·73 | vw | 3·77 | w | 3·36 | w |
| 3·57 | s | 3·52 | w | 2·57 | s |
| 3·50 | vw | 3·33 | vs | 2·50 | s |
| 3·31 | vs | 3·19 | fw | 2·36 | s |
| 3·19 | w | 3·12 | vw | 2·30 | s |
| 2·96 | fw | 2·99 | m | 2·00 | m |
| 2·84 | w | 2·85 | fw | 1·953 | w |
| 2·76 | w | 2·78 | fw | 1·848 | w |
| 2·54 | m | 2·57 | w | 1·794 | w |
| 2·47 | vw | 2·55 | s | 1·670 | s |
| 2·37 | fw | 2·48 | w | 1·623 | m |
| 2·31 | fw | 2·46 | w | 1·547 | w |
| 1·976 | m | 2·38 | w | 1·493 | s |
| 1·503 | w | 2·23 | vw | | |
| 1·500 | w | 2·19 | vw | | |
| | | 2·12 | w | | |
| | | 1·984 | vs | | |

a pure state, or of such large particle size. The hydrous mica from Yorkshire fireclays closely resembles that isolated from South Wales shales and also from Sarospatak, Hungary.

Recent work by Brown and Norrish[1] suggests that hydroxonium ions can replace potassium in the muscovite lattice, and they classify hydrous micas on this basis. By applying similar calculations, the

TABLE III. Atomic cell configuration.

| | Micaceous mineral from Tong. | | Hydromuscovite A (Brammall, Leech, and Bannister). | | Illite 2 (Grim, Bray, and Bradley). | |
|---|---|---|---|---|---|---|
| Si ... | 6·163 | 8·00 | 6·1183 | 8·00 | 6·7495 | 8·00 |
| Al ... | 5·040 | — | 5·6467 | — | 4·0237 | — |
| Ti ... | 0·114 | | — | | 0·0522 | |
| | | 3·96 | | 3·97 | | 4·02 |
| Fe ... | 0·295 | | 0·1108 | | 0·6419 | |
| Mg ... | 0·196 | — | 0·0981 | — | 0·5572 | — |
| Ca ... | 0·147 | — | 0·0309 | — | 0·0230 | — |
| Na ... | 0·233 | | 0·1171 | | 0·0427 | |
| | | 2·20 | | 1·99 | | 1·85 |
| K ... | 0·962 | | 1·3547 | | 1·0226 | |
| H ... | 7·029 | 4(OH) | 5·5423 | 4(OH) | 6·2714 | 4(OH) |
| O ... | 25·005 | 20(O) | 24·5159 | 20(O) | 24·7566 | 20(O) |

[1] G. Brown and K. Norrish, Min. Mag., 1952, vol. 29, p. 929.

structure of the Yorkshire hydrous mica can be adduced. Table III gives the atomic configuration of the mineral in comparison with other hydrous micas.

In calculating the above formula for the micaceous mineral, better agreement is given by attributing the Ca ions to the dioctahedral layer rather than to the alkali or hydroxonium ion grouping.

### *Possible mechanism of formation.*

The mechanism of formation of hydrous mica is still a matter for conjecture. The mineral may be produced as a result of diagenic or authigenic processes. The micaceous minerals in the Yorkshire fireclays appear to be diagenic in character, i.e. arising from the breakdown of true mica. Close examination of the clay in bulk indicated that the thin mica flakes were oriented along the bedding planes, implying that the mineral was deposited in a similar form to its present state, and not formed in situ. There is always the possibility, however, that the mineral may have been formed authigenically at some geological period prior to its deposition in the Lower Coal Measures.

### *Conclusions.*

The micaceous mineral isolated from a Yorkshire fireclay has been shown to be a hydrous mica. Other samples of fireclays from many localities contain a similar mineral. Separation of these minerals is being effected and it is hoped to compare the properties of these hydrous micas from different geological horizons and at various positions along the same seam.

Single crystal X-ray photographs are now being examined with a view to the complete elucidation of the structure.

# *High-order plates for the microscopic examination of mineral grains.*

By Frank Smithson, D.Sc.

University College of North Wales, Bangor.

[Taken as read March 26, 1953.]

FOR the examination of grains with high birefringence the usual types of wedge or plate often fail to give clear indications of optical sign. In such cases plates up to the 20th order on Newton's scale (relative retardation about 10$\mu$) may be employed.

*Determination of sign of length of a crystal*—A detrital crystal of zircon (length positive, i.e. slow) about 300–400$\mu$ thick observed between crossed nicols in conjunction with a 15–20th-order plate will illustrate this test. When the length of the crystal is parallel to the fast direction of the plate (fig. 1 *A*) there is compensation, and colour bands are seen. Without the plate, or with the crystal rotated through 90° (fig. 1 *B*), only high-order whites are seen. A crystal of high birefringence with length negative (e.g. a bipyramid of anatase) will give colour bands in position *B*, and none in position *A*.

*Determination of sign of an interference figure.*—In the eccentric figure of a cleavage flake of calcite (uniaxial negative) the brushes are usually clear, but the rings, having very high-order colours, are indistinct. The insertion of a high-order plate causes the rings to become distinct in two opposite quadrants, where high-order whites have been reduced to low-order colours; whereas in the other two quadrants the rings are undetectable, having been raised to still higher orders (fig. 2). A positive uniaxial figure will give rings in position *B*, but none in position *A*.

*Preparation of the plates.*—The plates are most readily made from sheets of clear selenite. Orientation is found on a thinned edge and strips in the fast direction are cut with a sharp blade. Suitable thickness is obtained by cleaving or building up. The order of the plate is found by making one corner wedge-shaped and counting the reds, or, for thicker plates, by cleaving a portion of it and determining the order of each flake. Alternatively, if a spectroscope attachment is available, the spectrum of the light transmitted by the plates when viewed between crossed nicols indicates their thickness. A plate of about the 10th-order gives seven dark bands in the visible spectrum, one of about the

15th-order shows ten, and one of about the 20th-order shows thirteen. The strips are mounted with Canada balsam between glass slips (usually

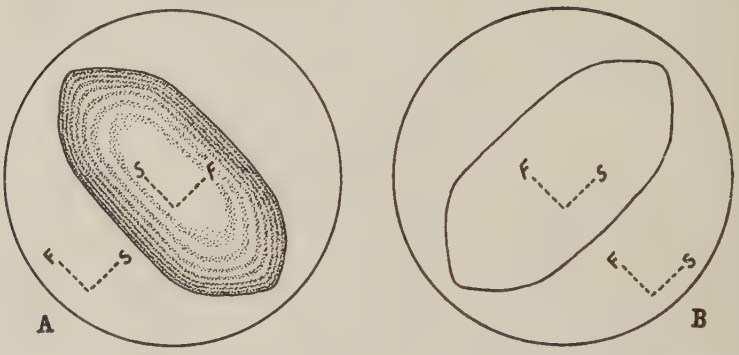


Fig. 1. Zircon between crossed nicols, using high-order plate.
F, S—fast and slow vibration-directions of the plate.
*F*, *S*—fast and slow vibration-directions of the zircon.

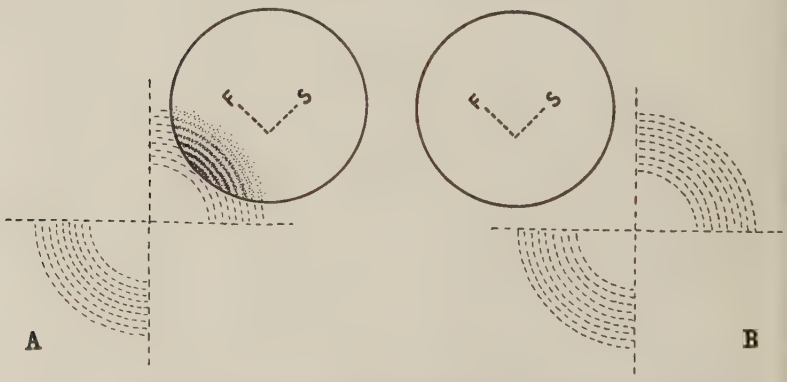


Fig. 2. Interference figure of calcite cleavage flake, using high-order plate.
F, S—fast and slow vibration-directions of the plate.

$12 \times 75$ mm.) to fit into the slot of the microscope. The baking must be gentle, since excessive heat damages the selenite.

High-order plates have also been prepared from rock-crystal by cutting slices parallel to the *c*-axis and grinding disks of appropriate thickness, which, enclosed between small cover-slips, are oriented in metal holders such as are supplied with the Leitz microscope.

It is convenient to prepare a set of three or four plates of different thicknesses, and when applying the test to try them in sequence until a clear result is obtained.

# *The relation between area and volume in micrometric analysis.*

By F. Chayes

The Geophysical Laboratory, Carnegie Institution of Washington, U.S.A.

[Communicated by Dr. S. J. Shand; taken as read March 26, 1953.]

In a recent note in this Magazine, Dr. R. B. Elliott[1] points out that inclined contacts of grains of considerably different index may bias the result of a micrometric analysis. That there may be some bias of this sort is hardly to be doubted, though I am inclined to feel that he greatly overestimates its importance. His demonstration, however, involves a fallacy so long and widely held as to be worth refuting.

Dr. Elliott begins by arguing that the micrometric analysis is an attempt to estimate directly the composition of the volume of rock actually contained in the thin section. The thickness of a thin section, however, has nothing to do with the question of whether the 'composition' of its surface may be regarded as an unbiased estimate of the composition of a volume of rock. The section could be wedge-shaped, hemispherical, or as thick as the lithosphere, provided only that we could satisfactorily identify the minerals whose sections form its surface.

The theoretical justification for 'Rosiwal' analyses as now performed has nothing to do with either thin sections or grain-size. The systematic traversing of the surface of the section is a form of graphical integration which may be made as precise as seems desirable. Of course this capacity for infinite improvement is mostly theoretical. One of the advantages of the point-counter[2] is that its error is well enough known to permit intelligent adjustment of count length to meet varying demands. The situation is by no means as clear for the various line-integrators, particularly the mechanically operated ones. In principle, however, it ought to be similar; the smaller the intervals between traverses the smaller the precision error of the results. But the question of precision is not a serious consideration at this stage of the argument. What matters here is that, barring identification difficulties (and erratic mechanical failure of the automatic integrators), the Rosiwal analysis is accurate *in the sense that it is unbiased.* If we can identify the mineral

[1] R. B. Elliott, Min. Mag., 1952, vol. 29, p. 833.

[2] F. Chayes, Amer. Min., 1949, vol. 34, pp. 1 and 600. [M.A. 11–277.]

sections forming the surface of the thin section, the micrometric analysis gives an unbiased estimate of their areal proportions, the 'composition' of the area.

But of what use are accurate areal proportions if we may not regard them as statements of composition by volume? Clearly they are of no use, and it is precisely in the passage from area to volume that most of the difficulty in interpreting Rosiwal analyses arises. The justification is simple, but, like the preceding argument, has nothing to do with rocks or the sizes and shapes of grains. It is just the usual formula, proved in every calculus text, for the volume of a solid, namely:

$$V = \int_a^b Adh \tag{1}$$

where $A$, the area of the cross-section perpendicular to an axis along which $h$ is measured, is some function of $h$. In order to operate mathematically with (1) it is necessary to know this function, but the formula is valid so long as the function exists, whether we know it or not. If $a$ and $b$ represent the top and bottom of the grain normal to the plane of the thin section, $A$ has one and only one value for every value of $h$ between $a$ and $b$. It follows then that if distances of $a$ (or $b$) from the plane of the thin section are equally likely, the proportion of the area of any section occupied by the grain is an unbiased estimate of its relative volume, for the sum of an infinite number of such infinitely thin areas would *be* its volume.

In practice, of course, the plane of the thin section cuts each grain only once, and a single cross-section, though accurate in the sense of being unbiased, will almost certainly be highly imprecise. For practical purposes we are forced to make assumptions about the distribution of grains through the mass. The problems are many and varied, and some of them are extremely complex. But neither the thickness of the thin section nor the volume of the rock it contains has anything to do with the passage from the determination of relative areas to the estimation of relative volumes. In particular, the temptation to identify its thickness with the differential and its volume with the quantity $Adh$ of equation (1) is to be scrupulously avoided.

Dr. Elliott's calculations are all based on the assumption that the micrometric analysis is an attempt to estimate directly the volumetric composition of the thin section, and the measuring procedure he follows is quite evidently influenced by this assumption. He says, for instance, (p. 833), that when contacts are inclined and adjacent grains differ

considerably in index, '. . . we measure the maximum diameter of the high relief mineral, that is, from the tip of the bevelled edge on one side to the tip of the bevelled edge on the other. This will produce an inaccuracy, *for we ought to measure from the centre of the bevel on one side to the centre of the bevel on the other*' [italics added]. But according to the preceding argument, this last is just precisely what we should *not* do. The proper procedure is to focus as sharply as possible on the surface of the slide and change keys when the intersection of the grain contact with the slide surface passes the cross-hair intersection. In general, only that part of any grain which does actually reach the surface along the line of traverse is to be measured or counted.

This procedure is an exact analogue of that originally proposed by Delesse[1] more than a century ago. He says (p. 384) 'On doit avoir soin de dessiner seulement les minéraux qui trouvent dans le plan même de section', and again, on the same page, '. . . on ne dessine que celles qui sont réellement coupées par la surface considérée.' Precedent for supposing that micrometric measurement is in some way concerned with a volume rather than a surface may be found in Rosiwal (p. 163),[2] but the notion is quite as unwarranted today as it was in 1898.

When the intersections of grain boundaries with the surface of the section can be clearly located, the bias described by Dr. Elliott simply does not exist if the measurement is properly made. The combination of high relief, fine grain, and inclined contacts—sometimes even any one of the three—may make it difficult or impossible to locate the intersections of contact planes with the surface of the section. Though the resulting uncertainty has nothing whatever to do with the relation between area and volume, it may influence our ability to measure the area in either of two ways. It may simply lower the precision of the measurement without affecting its potential accuracy; when this is so the obvious remedy is more extensive measurement if the loss of precision cannot be tolerated. If we have reason to suppose, however, that the error does introduce a systematic bias into the areal measurement, mere extension of the measurement will not help. If the bias can be neither tolerated nor eliminated, the material is not amenable to micrometric analysis. The failure, however, is not in the fundamental relation between areal and volumetric composition, as one might suppose from Dr. Elliott's treatment of the problem. It is simply our inability to obtain an unbiased estimate of the composition of the area.

[1] A. Delesse, Annales des Mines, 1848, sér. 4, vol. 13, p. 379.

[2] A. Rosiwal, Verhandl. Geol. Reichsanst. Wien, 1898, vol. 5-6, p. 143.

# *X-ray investigation of hillebrandite.*

By L. Heller, B.A., Ph.D.

Birkbeck College Research Laboratory, University of London.

[Communicated by Dr. J. W. Jeffery; read January 22, 1953.]

HILLEBRANDITE was first characterized by Wright[1] as a white, fibrous mineral with the composition $2CaO.SiO_2.H_2O$, optical properties $\alpha_{Na}$ 1·605±0·005, $\gamma_{Na}$ 1·612±0·003, moderately weak birefringence, parallel extinction, optic axial angle 2E between 60 and 80°, and density 2·692. X-ray powder data were first published by Vigfusson,[2] but these have not been substantiated by later investigators (Clark and Bunn,[3] McMurdie and Flint,[4] and Heller and Taylor[5]). Synthetic dicalcium silicate $\beta$-hydrate has been found to resemble hillebrandite closely.

The present sample of hillebrandite from Velardeña, Durango, Mexico, was kindly supplied by the Building Research Station. It consisted of short, white fibres with optical properties compatible with those described by Wright. The hillebrandite fibres were associated with hibschite, identified optically ($n$ about 1·67), and with wollastonite, identified optically and by X-rays.

The results of a chemical analysis of the present sample are shown in table I. If it is assumed that all the $CO_2$ is present as calcite, that the sample contains hibschite, wollastonite, and gypsum, and that Al replaces Si, and all other cations replace Ca, the resulting composition of hillebrandite approximates to $Ca_2SiO_4.H_2O$ (column 2b).

The density of the sample was found to be 2·69. The density of the lighter fraction of a sample separated once with liquid of specific gravity about 2·70 and boiled to eliminate occluded air was 2·67. The corrected density, allowing for the presence of calcite, hibschite, and wollastonite, is 2·66.

[1] F. E. Wright, Amer. Journ. Sci., 1908, ser. 4, vol. 26, p. 551.

[2] V. A. Vigfusson, Amer. Journ. Sci., 1931, ser. 5, vol. 21, p. 74. [M.A. **5**–45.]

[3] L. M. Clark and C. W. Bunn, Journ. Soc. Chem. Industry, 1940, vol. 59, p. 155. [M.A. **8**–116.]

[4] H. F. McMurdie and E. P. Flint, Journ. Res. Nat. Bur. Standards, U.S.A., 1943, vol. 31, p. 227. [M.A. **9**–45.]

[5] L. Heller and H. F. W. Taylor, Journ. Chem. Soc. London, 1952, p. 2535. M.A. **12**–83.]

TABLE I. Chemical analyses of hillebrandite.

| | 1. | 2. | 2a. | 2b. | 2c. | |
|---|---|---|---|---|---|---|
| $SiO_2$ ... | 32·59 | 30·49 | 30·71 | 0·511 | Si(Al) ... | 12·3 |
| $Al_2O_3$ ... | 0·23 | 2·16 | 1·26 | 0·012 | Ca, &c. ... | 24·0 |
| CaO ... | 57·76 | 56·13 | 57·75 | 1·030 | O ... ... | 48·2 |
| $TiO_2$ ... | 0·02 | 0·01 | 0·01 | — | $H_2O$ ... | 12·1 |
| $Fe_2O_3$ ... | 0·15 | 0·28 | 0·32 | 0·002 | | |
| MnO ... | 0·01 | 0·03 | 0·03 | — | | |
| MgO ... | 0·04 | 0·28 | 0·32 | 0·008 | | |
| $Na_2O$ ... | 0·03 | 0·02 | 0·02 | — | | |
| $K_2O$ ... | 0·05 | 0·07 | 0·08 | 0·001 | | |
| $CO_2$ ... | — | 1·12 | — | — | | |
| $SO_3$ ... | — | 0·19 | — | — | | |
| $H_2O-$ ... | 9·36 | 0·14 | — | — | | |
| $H_2O+$ ... | | 8·80 | 9·50 | 0·527 | | |
| | 100·24 | 99·72 | 100·00 | | | |

1. Hillebrandite, Terneras mine, Velardeña, Durango, Mexico. Analyst, E. T. Allen (F. E. Wright, loc. cit.). Total iron as $Fe_2O_3$.
2. Hillebrandite, Velardeña, Durango, Mexico. New analysis by F. J. McConnell, Building Research Station. $H_2O+$, loss at 110–950° less $CO_2$.
2a. Column 2 after deducting impurities: 2·54 % calcite, 0·42 % gypsum, 4·4% wollastonite, and 4·4 % hibschite ($Ca_3Al_2Si_2O_8(OH)_4$), and adjusted to 100%.
2b. Column 2a expressed in molecular ratios.
2c. Unit-cell contents.

The crystallites composing the hillebrandite fibres were fairly well alined in the fibre direction but otherwise showed random orientation. J. D. Bernal and N. Joel, working on some of the fibres, had previously determined the unit-cell dimensions as: $a$ 16·32, $b$ 3·63, $c$ 11·84 Å., $\alpha = \beta = \gamma = 90°$ (private communication).

In the course of the present investigation one single crystal of hillebrandite was found among the fibres. It was needle-shaped, about $85 \times 20 \times 20\,\mu$ with straight extinction and positive elongation. Oscillation, rotation, and Weissenberg photographs were taken. The rotation photographs about the needle-axis were entirely compatible with rotation photographs of the fibres about the fibre-axis, which in turn were in good agreement with the powder data obtained from samples of the crushed material. The latter were the same as those previously described (Heller and Taylor, loc. cit.) and are reproduced here in table II. The line at 2·70 Å. was observed to vary in intensity and is therefore attributed, at least partly, to the presence of another substance and corresponds to the strongest line of hibschite.[1] The strongest lines of wollastonite and calcite could not be detected.

The unit-cell dimensions deduced from this crystal were $a$ 16·60,

[1] A. Pabst, Amer. Min., 1942, vol. 27, p. 783. [M.A. 8–359.]

TABLE II. X-ray powder data of natural hillebrandite.

| $d$ (Å.). | Int. | $d$ (Å.). | Int. | $d$ (Å.). | Int. | $d$ (Å.). | Int. |
|---|---|---|---|---|---|---|---|
| 8·2 | mw | 2·45 | w | 1·64 | w | 1·360 | vvw |
| 6·7 | vw | 2·37 | s | 1·62 | mw | 1·350 | vvw |
| 5·8 | w | 2·26 | ms | 1·61 | mw | 1·335 | vvw |
| 4·76 | vs | 2·23 | ms | 1·57 | mw | 1·325 | w |
| 4·06 | mw | 2·10 | vvw | 1·56 | vvw | 1·300 | vvw |
| 3·52 | mw | 2·06 | ms | 1·54 | w | 1·280 | vvw |
| 3·33 | vs | 1·96 | ms | 1·530 | vw | 1·220 | vvw |
| 3·02 | s | 1·93 | m | 1·525 | vw | 1·205 | vvw |
| 2·92 | vvs | 1·87 | ms | 1·505 | vvw | 1·190 | w |
| 2·82 | s | 1·85 | m | 1·500 | vvw | 1·180 | w |
| 2·76 | s | 1·81 | s | 1·470 | w | 1·175 | w |
| 2·70 | w* | 1·75 | m | 1·450 | vw | 1·120 | vw |
| 2·67 | w | 1·72 | mw | 1·430 | vw | 1·115 | vvw |
| 2·63 | mw | 1·69 | vvw | 1·415 | vw | 1·095 | vw |
| | | 1·67 | vvw | 1·365 | vvw | | |

* This line varied in intensity for different samples taken from the same lump of mineral. It corresponds to the strongest line of hibschite.

$b$ 7·26, $c$ 11·85 Å., $\alpha = \beta = \gamma = 90°$. The $b$(needle)-axis showed strong pseudo-halving. Reflections on the weak layer-lines were streaks elongated in the direction of the layer-lines. It was not possible to detect these reflections on photographs of an imperfectly oriented fibre, which accounts for Bernal and Joel's value of 3·63 Å. for the length of the $b$-axis.

Using the analysis and density previously deduced, it follows that the number of formula-units of $2CaO.SiO_2.H_2O$ per cell is 12·1 (column 2c of table I) or 12 in the ideal case.

The determination of the true structure of hillebrandite can be simplified as a first approximation by considering only the pseudo-structure which is obtained when the weak intermediate layer-lines in the $b$-direction are neglected. The layer-lines are so weak that the pseudo-structure cannot differ substantially from the true structure.

A complete set of oscillation photographs was taken about the $b$-axis and sufficient oscillation photographs about the $c$-axis to estimate all the $0k0$ reflections. Weissenberg photographs were also taken of the $h0l$, $h2l$, and $h4l$ zones. (Photographs of the weak zones $h1l$ and $h3l$ would have required excessively long exposures.) The series of oscillation photographs about the $b$-axis show that there is a plane of symmetry perpendicular to $b$ for all the reflections. For the pseudo-structure there are also planes of symmetry perpendicular to the other two axes.

This is confirmed by the Weissenberg photographs. For the true structure, however, there is some evidence that there may be no further planes of symmetry. On two successive photographs, both of which show the $(11\bar{2})$ and $(11\bar{3})$ reflections together with reflections (112) and (113), the former were respectively stronger than the latter. (These indices refer to the true cell.) As these reflections are streaks, however, the difference in intensity may also be due to a cutting-off effect. The symmetry of the true structure may therefore be monoclinic (with a $\beta$ angle of 90°), but the evidence is ambiguous. The pseudo-structure is orthorhombic.

The following are the only systematic absences observed for the true structure: $h0l$ reflections absent for $h$ odd and $0k0$ reflections for $k$ odd. The space-group is therefore compatible with $P2_1/a$. This is, however, subject to some uncertainty, due to the weakness and streakiness of the reflections on the intermediate layer-lines.

For the pseudo-structure, in which $b$ 3·63 Å., the following are the only observed systematic absences, $hkl$ reflections absent for $h+k$ odd and $0kl$ reflections for $k$ odd or $l$ odd, with the only observed exception of (001), which is very weak. (These indices, of course, refer to the pseudo-cell.) Although this reflection was observed on oscillation and rotation photographs of the single crystal and of fibres, and also on powder photographs of hillebrandite and of synthetic dicalcium silicate $\beta$-hydrate, and therefore appears to be genuine, it is so weak that its presence cannot indicate a significant departure from the space-group otherwise deduced. The absences, neglecting the (001) reflection, are characteristic of space-groups $Ccmm$, $Ccm2$, and $Cc2m$. These space-groups have 16-fold general, and 8- or 4-fold special positions. The pseudo-cell of hillebrandite contains 6 silicon and 30 oxygen atoms. It is therefore not apparent how the cell content may be reconciled with the observed space-group. This problem requires elucidation.

Hillebrandite is one member of a series of hydrated calcium silicates which resemble each other and the anhydrous mineral wollastonite in crystallizing with a fibrous habit, and in having a repeat distance of 7·26 Å. with strong pseudo-halving in the needle or fibre direction. These have been described by Bernal,[1] who also discussed the possible significance of the strong 3·65 Å. repeat distance. However, it appears from the present results that the occurrence of the weak, intermediate layer-lines and the type of stacking disorder indicated by the streakiness

[1] J. D. Bernal, Proceedings of the Third International Symposium on the Chemistry of Cements, London, 1952, in the press.

of the reflections on these layer-lines cannot be ignored even as a first approximation.

A Patterson map in the (010) projection was calculated for hillebrandite, but was not found very helpful at this stage. It was therefore decided to postpone further attempts at interpreting the structure, pending a thorough reinvestigation of the structure of wollastonite which is in progress in this laboratory.

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